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Studies on Salt Solution Aerosols. V.[1] The Effect of Surface Active Substance upon the Droplet Size of an Aqueous NaCl Solution Aerosol

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An aqueous NaCl solution (10%) containing a surface active substance was dispersed to a mist with a Dautrebande type atomizer. The influence of the surface active substance on the droplet size and mass concentration of the mist during aging was studied. We examined ethyl alcohol, acetic acid, ethyl acetate, acetone, glycerine, and a commercial nonionic surfactant. From the results it was found that at an early stage of aging, the droplet number present in mist was inversely proportional to the fourth power of droplet size.

In a previous study,[2] we carried out an experiment on the production of aqueous NaCl solution aerosols by atomizing an aqueous NaCl solution containing or not containing a surfactant with an atomizer. We found that the droplet size decreases with the increase of the concentration of the surfactant or with the decrease of the surface tension of the dispersing solution. Surfactants used were commercial products of polyoxyethylene nonylphenyl ether, $C_9H_{19}C_6H_4O(CH_2CH_2O)_nH$ with $n=6$, 9, and 21.

In the present study we worked with a Dautrebande's baffle type atomizer, which is superior to the intercepting glove type used earlier as it produces droplets finer than 1.2 μ diameter.

Unlike the above-mentioned polymeric surfactants with the c.m.c. ranging from 10^{-1} to 10^{-2}% by weight, almost all the surface active substances examined in the present work are of much higher solubility so that they enabled us to conduct the experiment over a wider range of concentration to gain knowledge of the role of surface active substance in the production of mist and, moreover, of the correlation between the size and number of the droplets present in mist immediately after its formation.

Various methods[3] of measuring the size of droplets of a mist have been presented, but they are laborious and troublesome on account of the volatility of the droplets causing alteration in their size. For example, in the chemical spot method,[3] it involves preparation of a series of calibration curves. The method adopted in the present study takes advantage of the volatility and is of significance as being applicable and available to much the same extent as the other methods.

Experimental

Materials. Ethyl alcohol, acetic acid, ethyl acetate, acetone, and glycerine used were of the extra pure grade. Commercial surfactant, EA-80 (polyoxyethylene nonylphenyl ether, $n=9$), was used as obtained from a chemical supply house.

Apparatus and Procedure. The over-all experimental

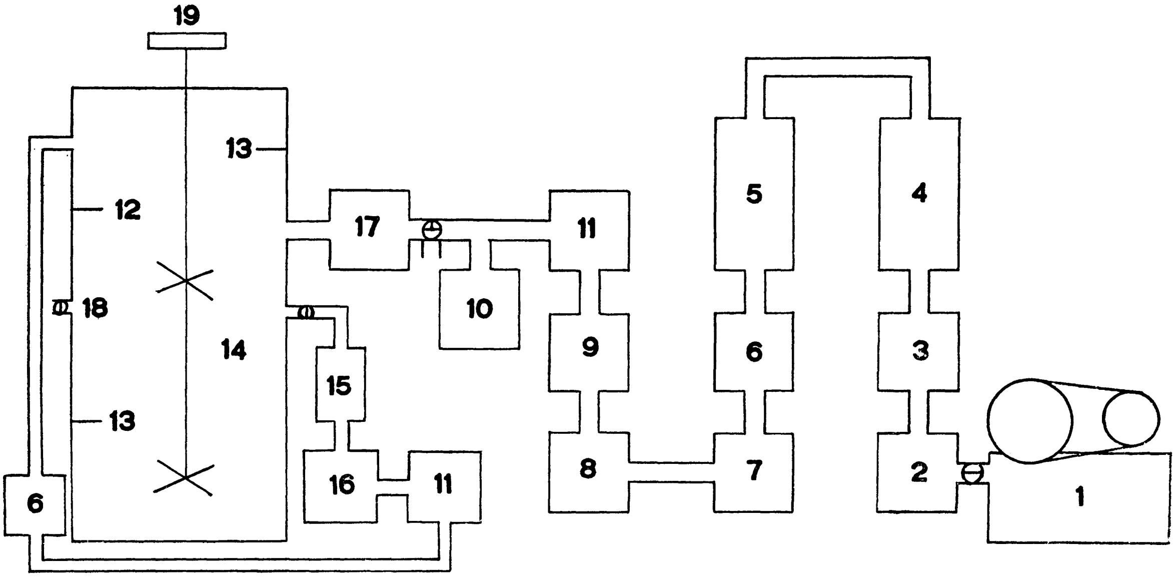

Fig. 1. Over-all experimental arrangement.
1) compressure 2) air cleaner 3) pressure regulator 4) tubes of glass fibers 5) tubes of absorbent cotton 6) bubbling bottles for humidification 7) large bottles for air buffering 8), 9) pressure regulators 10) manometer 11) flowmeter 12) hygrometer 13) glass thermometer 14) chamber 15) electrical precipitator 16) air pump 17) atomizer 18) sampling hole 19) stirrer.

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[1] Part IV: This Bulletin, **44**, 637 (1971).

[2] I. Sano, S. Hikita, and Y. Ueno, *Nippon Kagaku Zasshi*, **90**, 876 (1969).

[3] Y. Ueno and I. Sano, This Bulletin, **44**, 637 (1971).

arrangement is illustrated in Fig. 1. The compressed air at 5 kg/cm^2 (1) was driven through an air cleaner (2) and its pressure was reduced to 3 kg/cm^2 by a pressure regulator (3). The air was passed through filter tubes of glass fibers (4) and of absorbent cotton (5) for elimination of air-borne dust and then, it was humidified by bubbling through the same solution (6) as that to be dispersed and released from gustiness of flow with the aid of two large bottles (7). Finally, the pressure was adjusted and maintained constant at 2 kg/cm^2 by regulators (8) and (9). The mist thus generated with an atomizer (17) was introduced for 10 min into a mist chamber which had previously been saturated with water vapor of the dispersing solution. The humidity and temperature in the chamber were measured by means of an electrical resistance type hygrometer (12) and a glass thermometer (13) before and after the run. The temperature was kept at 20.0°±0.5°C throughout all the runs of experiment. The mist was subjected to aging with a constant rate stirrer (50 rev/min) (19) for an hour. The recorded time was reckoned from the moment of stopping the introduction of mist. At frequent intervals, portions of the mist were drawn for determination of mass concentration and particle size. The total amount of the portions of mist drawn from the chamber, so that it would scarcely affected the accuracy of the determination.

The solution to be dispersed was an aqueous NaCl solution (10%) or that containing a surface active substance in such an amount that the diminution of NaCl was within 0.05%.

Mist Generator. The mist generator employed is a modification of the Dautrebande type[4] and is illustrated in Fig. 2. The amount of the dispersing solution present in the generator is maintained constant by feeding fresh solution from the bottom of a cylindrical reservior (7) of 7 cm diameter, and the excess leaves the generator to a sink through a level tube (not shown in Fig. 2) whose height is adjustable as one wishes. The solution is drawn up by virture of the Venturi effect through the annular channel between the nozzle (3) and the filtering column (4). The atomized droplets impinge against the upper part of the filtering cap (5); the coarser ones are unstable to precipitate and run down into the dispersing solution (10), while those surviving are driven to pass through about fifty, small holes of 1.0 mm diameter (8) in the filtering column (4) and some of them encounter one another and coalesce. The stabilized and finer mist is thus generated through a mouthpiece (6).

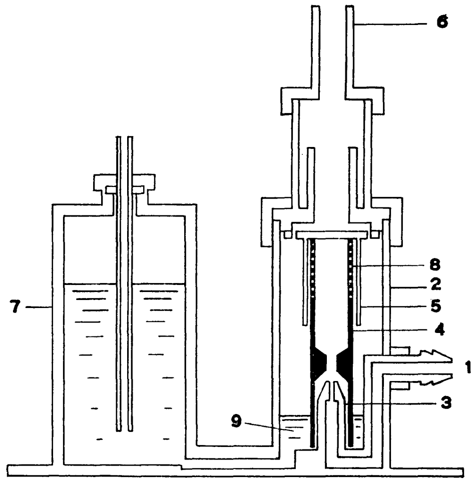

Fig. 2. Aerosol generator equipped with a constant feeding reservior.
1) compressed air tubing 2) plastic cylinder 3) air nozzle 4) filtering column topped by filtering holes 5) filtering cap 6) mouthpiece 7) reservior 8) small holes of 1.0 mm diameter in filtering column 9) dispersing solution

It is well known that this device can favourably be utilized for generation of submicronic droplets on account of its merit that size selection is effectively made through a liquid filtration mechanism, whereby coarser droplets are obligatory removed from the mist in the inner column.

Mass Concentration Analysis. Portions of the mist were periodically drawn with a constant rate air pump and passed through an electrical precipitator under a voltage of 7200 V/cm. The deposit in it was dissolved in 20 cc of distilled water and the weight was determined by electrical conductivity measurement with an error of less than 5%. With the volume of the mist drawn, which was recorded on the flowmeter, the concentration was calculated as milligrams of NaCl per cubic centimeter.

Particle Size Analysis. Portions of the mist were drawn into a silica gel holding syringe and dried, and they were passed to a precipitator at a rate of 15 cc/min. The precipitator used was that of Shibata Scientific Instrument Co. Estimates of the particle size were made on the thermal precipitator samples with a Hitachi HU-11DS electron microscope at a magnification of 3000 X. Electron microscope collodion mesh grids were mounted on a circular cover glass which was fitted close to a heated wire of the thermal precipitator. The sodium chloride particles were cubic crystals, and the number averaged width of their one crystal face was regarded as the representative size. From the average width (L) thus found, we calculated the radius (R) of the sphere corresponding to a 10% solution droplet.

Results and Discussion

Time Variation of Mass Concentration. Figure 3 shows that the mass concentration decreases with the

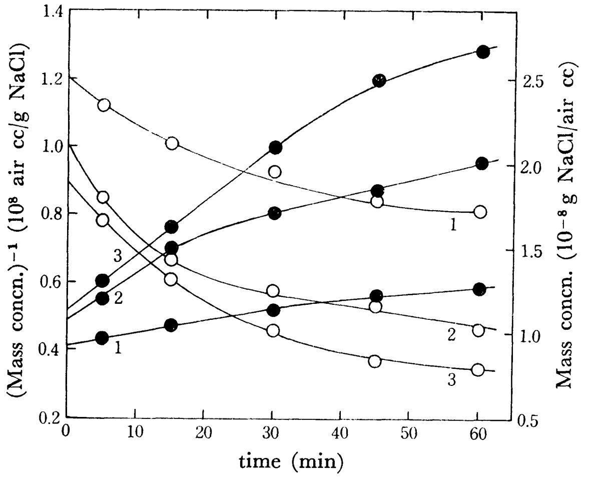

Fig. 3. Time variation of mass concentration.
(1) with no surface active substance
(2) acetone, 0.25 mol/l
(3) acetone, 0.50 mol/l solid circles refer to the left-hand axis and open circles the right one.

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[4] L. Dautrebande, H. Beckmann, and W. Walkenhorst, *Arch. intern. Pharmacodynamide*, **66**, 170 (1958); L. Dautrebande, "Microaerosols," Acad. Press, London and New York (1962); W. Walkenhorst and L. Dautrebande, *Staub.*, **24**, 505 (1964); M. J. Matteson and M. Stober, *J. Colloid & Interface Sci.*, **23**, 203 (1967); M. Suzuki, S. Watanabe, S. Hongo, and T. Ohata, *Zairyo*, **17**, 564 (1968).

elapse of time and markedly with the addition of a surface active substance to the dispersing solution. It will be seen that if the reciprocal of the mass concentration is plotted against the time, a linear relation holds in the early stages of nearly all the runs, revealing that the rate of the decrease in mass concentration follows the rate law of a second order reaction.

Time Variation of Particle Size Distribution and Number Concentration. The variation in particle size distribution with time is given in Fig. 4. It is evident in the figure that the size of a sodium chloride particle as represented by the width of one crystal face increases with time and, with the particles obtained from the solution droplets containing ethyl acetate, the size gets smaller as the surface active substance is more concentrated. The similar results were found for another surface active substances such as ethyl alcohol, acetic acid, acetane, glycerine, and polyoxyethylene nonylphenyl ether.

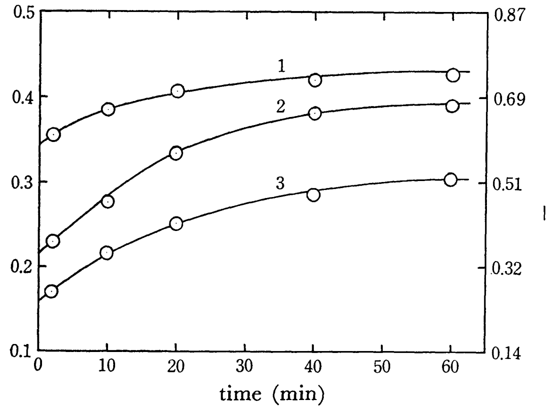

Fig. 4. Time variation of particle size distribution.
(1) with no surface active substance (2) ethyl acetate, 0.20 mol/*l* (3) ethyl acetate, 0.45 mol/*l*

We calculate the average droplet radius ($\bar{R}_t$) from the average crystal size ($\bar{L}_t$) by use of the relation

$$4/3\cdot\pi\bar{R}_t^3\cdot\rho_1\cdot W/100 = \rho_2\bar{L}_t^3 \tag{1}$$

where W is the NaCl concentration of dispersing solution, ρ_1 and ρ_2 are the densities of the solution and NaCl crystal, respectively, and the subscript t is the time elapsed, while the bar over a letter signifies the average. On the right axis in Fig. 4 is shown the radius (R_t).

Size Distribution and Number Concentration Immediately after Atomization. Let us express the average of crystal size, droplet radius, mass concentration, and number concentration at zero time by L_0, R_0, C_0, and N_0, respectively. The value of L_0 or R_0 is found by extrapolation of the plot of L_t or R_t *vs.* t to the intercept in Fig. 4 and similarly the value of C_0 in Fig. 3. The number concentration N_0 can be estimated by

$$N_0 = C_0/(L_0^3\rho_2) = C_0/(4/3\cdot\pi R_0^3\rho_1\cdot W/100) \tag{2}$$

Figure 5 indicates the relationship between the droplet radius (R_0) or number concentration (N_0) and the surface tension of dispersing solution. From the figure, it will be noted that as the surface tension is decreased, the smaller radius and the higher concentration are attained except the case of glycerine which exhibits that the plotted points deviate largely from the curves for the radius as well as the concentration probably because of comparatively high viscosity of the solution. Figure 6 shows the relationship of R_0 or N_0 and the viscosity, with the exception of the solutions of EA-80 and ethyl acetate which are of low viscosity. Remark should be made, here, of the fact that the relation of R_0 to the viscosity is in the reverse to that in the previous paper;[5] the reason may be possibly be that the working mechanism of the present atomizer is different from that of the atomizer employed previously. We will later report the effect of viscosity in more detail with particular reference to the experiments using glycerine, ethylene glycol and so on as a surface active substance.

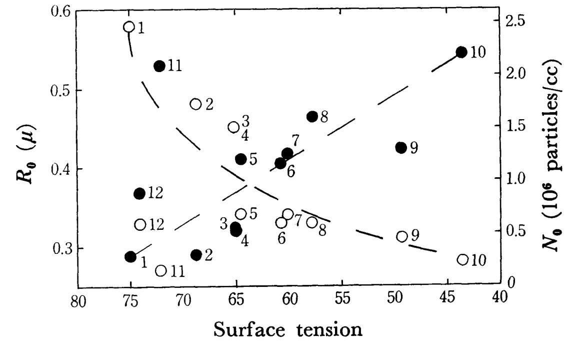

Fig. 5. Relation between R_0 or N_0 and the surface tension of dispersing solution.
(1) with no surface active substance (2) acetic acid, 0.25 mol/*l* (3) ethyl alcohol, 0.25 mol/*l* (4) acetone, 0.25 mol/*l* (5) acetic acid, 0.50 mol/*l* (6) ethyl alcohol, 0.50 mol/*l* (7) acetone, 0.50 mol/*l* (8) EA-80, 10^{-2}% (9) ethyl acetate, 0.20 mol/*l* (10) ethyl acetate, 0.45 mol/*l* (11) glycerine, 1.00 mol/*l* (12) glycerine, 0.50 mol/*l* (○ : R_0, ● : N_0)

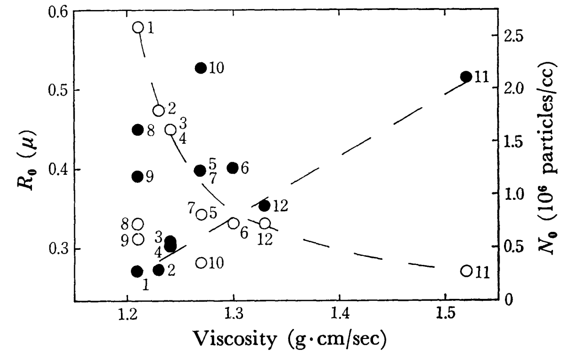

Fig. 6. Relation between R_0 or N_0 and the viscosity of dispersing solution.
With regard to the legends, confer Fig. 5. (○ : R_0, ● : N_0)

If it is assumed that a mechanical W is required for a large number of droplets, whose surface area taken together runs up to A_2, to be formed from a bulk solution of surface area A_1, then

$$W = \gamma\Delta A = \gamma(A_2 - A_1) \tag{3}$$

where γ is the surface tension. Neglecting A_1 in comparison with A_2 and denoting the surface active substance containing NaCl solution by a prime,

$$\gamma A_2 = \gamma' A_2' \tag{4}$$

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[5] I. Sano and Y. Ueno, *Nippon Kagaku Zasshi*, **90**, 47 (1969).

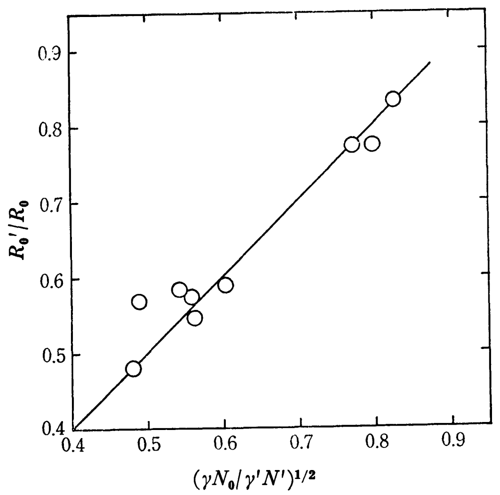

Fig. 7. Plot of R_0'/R_0 against $(\gamma N_0/\gamma' N_0')^{1/2}$.

and

$$\gamma'/\gamma = A_2/A_2' = N_0 S_0/N_0' S_0' \quad (5)$$

where N_0 and S_0 represent the number concentration of the droplets present in the mist chamber and the average area per droplet, respectively. Since S_0 is equal to $4\pi R_0^2$, it follows from Eq. (5) that

$$R_0'/R_0 = (\gamma N_0/\gamma' N_0')^{1/2} \quad (6)$$

The validity of Eq. (6) is as given in Fig. 7.

According to the results previously reported,[2)]

$$R_0'/R_0 = (a\gamma'^{1/2}-b)(a\gamma^{1/2}-b) \quad (7)$$

where a and b are empirical constants. From Eqs. (6) and (7), we get

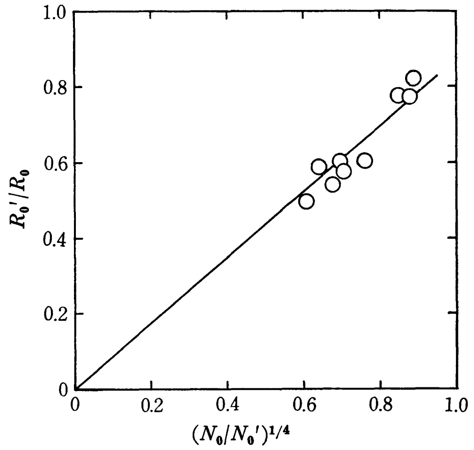

Fig. 8. Plot of R_0'/R_0 against $(N_0/N_0')^{1/4}$.

$$R_0'/R_0 = (N_0/N'_0)^{1/4}[(1-b/a\cdot\gamma'^{-1/2})/(1-b/a\cdot\gamma^{-1/2})]^{1/2} \quad (8)$$

The magnitude of the 1/2-power term of the right side is clearly less than unity as γ' is smaller than γ, and would be supposed to remain nearly constant for the range studied. Experimental verification of Eq. (8) is presented in Fig. 8; there is a straight line of a slope slightly lower than 45° which is in conformity with expectation. This reveals that the Eq. (8) might be approximated to

$$R_0'/R_0 = (N_0/N_0')^{1/4} \quad (9)$$

It will be a useful relation for the estimation of the droplet size or the number concentration in aerosol at zero time without knowledge of the surface tension of the solution to be dispersed.