BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 626—627 (1972)

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

Yasuo UENO and Isamu SANO

Department of Chemisty, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya

(Received November 20, 1970)

For the purpose of measuring the size distributions of aqueous sodium chloride solution aerosols, a new method based upon the chemical spot formation was developed.[2] One merit of the method is the easy preparation of a transparent film of polyvinyl alcohol containing the detecting reagent (silver nitrate) which reacts with the solution droplets to give spots of clear outlines. In addition a quantitative relationship holds between the size of the droplets and that of the spots impressed by them.

We have extended this technique to the size measurement of aqueous sodium sulfate solution aerosols. The results were analyzed in combination with those of aqueous sodium chloride solution aerosols.

Experimental

Materials. Ethanol used was of extra pure grade. Polyvinyl alcohol (PVA), obtained from Kurare Co., was 1700 in polymerization degree and 85% in saponification extent. Barium perchlorate was of chemical pure grade.

Preparation of the Reagent Film. To 100 g of an aqueous solution containing 4% by weight of PVA was added 200 m*l* of C_2H_5OH, and then a) 1 m*l*, b) 2 m*l* c) 3 m*l* and d) 4 m*l* of aqueous 40% $Ba(ClO_4)_2 \cdot 3H_2O$ solution was added separately to obtain four solutions of the detecting reagent in different concentrations. On dropping 10 μl of these solutions upon a dry glass slide[3] by means of a micropipette, the solvent (alcohol and water) rapidly evaporated off, leaving a circular transparent film of reagent, about 2.1 cm in diameter.

Generation of Droplets and Measurement of Size Distribution. An aqueous aerosol of 10% Na_2SO_4 solution was introduced into a mist chamber from an atomizer and was subjected to aging for various periods of time under agitation. The droplets were allowed to settle under the action of gravity onto the reagent film and an oil film[2] held on a glass slide. They were put side by side in the chamber. The size of the spots formed on the reagent film was measured with a phase microscope and that of the droplets suspended in the oil film with an ordinary microscope. Microphotographs of the spots and droplets were enlarged and their sizes were recorded with due precaution. The size of the droplets was in the range of about 0.3—12 μ in diameter.

Results and Discussion

Experimental Construction of the Calibration Curve. Both droplets and their spots have their own size distributions. 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 constructed for four films of varying $Ba(ClO_4)_2$ concentrations (Fig. 1, solid lines). We see that the spot diameter decreases with increasing reagent concentration in film.

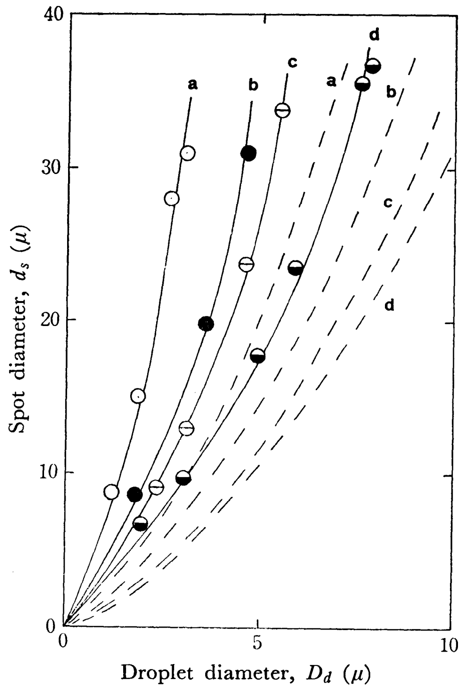

Fig. 1. Relation between the spot and droplet diameters. Solid lines refer to experimental curves and dashed lines calculated ones.
a : 1 m*l* $Ba(ClO_4)_2$ solution, b : 2 m*l* $Ba(ClO_4)_2$ solution
c : 3 m*l* $Ba(ClO_4)_2$ solution, d : 4 m*l* $Ba(ClO_4)_2$ solution

Calculation of the Calibration Curve. Assumptions similar to those of the former report[2] were made, *viz*, the spots of $BaSO_4$ formed are all of a cylindrical form whose height is equal to the film thickness. We thus obtain the relation

$$D_d{}^3 = 3/2\rho[\mathrm{Film}]C[\mathrm{Ba(ClO_4)_2}]M[\mathrm{Na_2SO_4}]Hd_s{}^2/(\rho[\mathrm{Na_2SO_4}]C[\mathrm{Na_2SO_4}]M[\mathrm{Ba(ClO_4)_2}]), \quad (1)$$

where ρ[Film]: density of film,
$\rho[Na_2SO_4]$: density of aqueous Na_2SO_4 solution,
$C[Na_2SO_4]$: concentration of aqueous Na_2SO_4 solution,
$C[Ba(ClO_4)_2]$: concentration of $Ba(ClO_4)_2$ in film,
$M[Na_2SO_4]$: molecular weight of Na_2SO_4,
$M[Ba(ClO_4)_2]$: molecular weight of $Ba(ClO_4)_2$,
H: thickness of film.

Since the concentration of the Na_2SO_4 solution used is known, Eq. (1) takes the form

1) Part V: Y. Ueno and I. Sano, This Bulletin, **44**, 908 (1971).
2) Y. Ueno and I. Sano, *ibid.*, **44**, 637 (1971).
3) cleaned beforehand in the same way as previously reported.[2]

TABLE 1. ESTIMATED VALUES OF ρ[Film], H AND $C[Ba(ClO_4)_2]$ AND THE VALUES OF ε.

Film	ρ[Film][a] (g/cm^3)	H[b] (μ)	$C[Ba(ClO_4)_2]$[c] (%)	$\varepsilon_{obs.}$	$\varepsilon_{calc.}$		
(a)	1.40	0.31_2	10.7	0.33	0.32[d]	0.33[e]	0.33[f]
(b)	1.48	0.33_1	19.0	0.42	0.41	0.40	0.40
(c)	1.55	0.34_9	25.7	0.45	0.46	0.46	0.46
(d)	1.61	0.36_8	31.2	0.52	0.51	0.51	0.51

a), b) and c) The values of ρ[Film], H and $C[Ba(ClO_4)_2]$ are calculated by the relations:
$\rho[\text{Film}]=(W[\text{PVA}]+W[Ba(ClO_4)_2\cdot 3H_2O])/(W[\text{PVA}]/\rho[\text{PVA}]+W[Ba(ClO_4)_2\cdot 3H_2O]/\rho[Ba(ClO_4)_2\cdot 3H_2O])$
$H=4(W[\text{PVA}]+W[Ba(ClO_4)_2\cdot 3H_2O]/\rho[Ba(ClO_4)_2\cdot 3H_2O])/\pi D_f^2$
$C[Ba(ClO_4)_2]=100W[Ba(ClO_4)_2\cdot 3H_2O]\cdot M[Ba(ClO_4)_2]/(W[\text{PVA}]+W[Ba(ClO_4)_2\cdot 3H_2O])M[Ba(ClO_4)_2\cdot 3H_2O]$
where W and ρ and the weight and density, respectively, of solid PVA or $Ba(ClO_4)_2\cdot 3H_2O$ in the film having a diameter D_f which is found to be 2.1 cm.
d) $k=1.0$, $\alpha=0.79_1$, $\beta=0.00015_5$. e) $k=2.0$, $\alpha=0.88_6$, $\beta=0.000056_3$. f) $k=5.0$, $\alpha=0.95_3$, $\beta=0.000019_4$.

$$D_d^3 = Kd_s^2 \tag{2}$$

where K is a constant given by

$$K = 5.82\rho[\text{Film}]HC[Ba(ClO_4)_2].^{4)} \tag{3}$$

According to Eq. (2), a plot of log D_d against log d_s should be linear, and this is actually the case, for all concentrations as shown in Fig. 2, the slope being 2/3 for all straight lines. The value of K is found from the intercept on the log D_d axis.

Theoretical curves calculated by Eq. (2) using the values listed in Table 1, are represented by dashed lines in Fig. 1. It is clear that the diameters of the spots found experimentally are larger than those calculated.

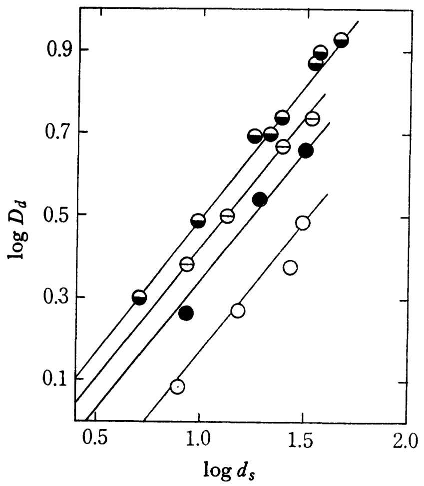

Fig. 2. Plot of log D_d against log d_s.
○: 1 ml $Ba(ClO_4)_2$ solution, ●: 2 ml $Ba(ClO_4)_2$ solution
⊖: 3 ml $Ba(ClO_4)_2$ solution, ◒: 4 ml $Ba(ClO_4)_2$ solution

Comparison between Theory and Experiment. It has been shown that for a given D_d[2)]

$$d_{s\ \text{theor.}}/d_{s\ \text{exptl.}} = (K_{\text{exptl.}}/K_{\text{theor.}})^{1/2} = \varepsilon \tag{4}$$

The values of ε determined by use of the values of $K_{\text{exptl.}}$ and $K_{\text{theor.}}$ in accordance with Eq. (4) are listed in Table 1 ($\varepsilon_{\text{obs.}}$). All of them are less than unity. For aqueous NaCl solution aerosols it has been shown[2)] that

$$\varepsilon = k(1-\alpha e^{-\beta C}) \tag{5}$$

where C is the concentration (%) of the detecting reagent ($AgNO_3$) in film. The applicability of Eq. (5) for aqueous Na_2SO_4 solution aerosols is shown in Table 1 ($\varepsilon_{\text{calc.}}$).

By combining the cases of $AgNO_3$[2)] and $Ba(ClO_4)_2$, we find that

$$\varepsilon = k(1-\alpha e^{-\gamma C/M}) \tag{6}$$

where M is the molecular weight of $AgNO_3$ or $Ba(ClO_4)_2$ and γ a constant.

4) The concentration of the dispersing solution is 10% by weight of Na_2SO_4. The term K, corresponding to $3/2\cdot M[Na_2SO_4]/(\rho[Na_2SO_4]C[Ba(ClO_4)_2]M[Ba(ClO_4)_2]$ in calculated to be 5.82, by replacing the values of 1.09 for $\rho[Na_2SO_4]$, 0.10 for $C[Na_2SO_4]$, 336.2 for $M[Ba(ClO_4)_2]$ and 142.0 for $M[Na_2SO_4]$. For the values of ρ[Film], H and $C[Ba(ClO_4)_2]$, *cf.* Table 1.