The Effect of Organic Vapors on the Stability of Aerosols

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It is a well-known fact that aerosols are unstable by nature. The particles decrease in number rapidly both by coagulation due to mutual collision and by sedimentation under the gravity. Therefore, it would be difficult to define the stability of an aerosol system by a mathematical expression, since it is affected by many factors which may be co-operative. In evaluating the stability of an aerosol system, the rate of decrease in i) the particle number concentration[1], or ii) the mass concentration[2] is mainly measured and, in some cases, iii) the decrease in optical density or iv) the sedimentation velocity of boundary surface of the system[3] is also observed. The method i) is most essential, but requires skillful techniques and elaborate operation; whilst, the methods ii) to iv) are applicable merely to a routine work.

The coagulation processes of aerosol particles obey Smoluchowski's theory concerning the relationship between the time elapsed and the number of particles of colloidal dispersions. In spite of the theory being based on the many assumptions, the equation has been widely used so it is convenient to adopt his coagulation constant as a measure of the stability of an aerosol system. However, few investigations along these lines are available though numeous reports have been published regarding the stability of aerosols.

It may be expected that, when a substance which exhibits a capillary activity is added to an aerosol, the rate of coagulation of the particles may be influenced both by the nature and the concentration of the admixture. If this is the case, it may offer a most interesting problem on the collision process of aerosol particles, since it has been generally believed that the collision efficiency of aerosol particles is equal to unity under normal circumstances[4].

In a previous paper the stabilizing effect of the vapors of such organic surfactants as lower series of mono-functional alcohols (C_1 to C_5), acetone and ethyl acetate has been established for the fog of aqueous ammonium chloride solution, but the detailed mechanism of the coagulation process delayed by these vapors has not yet been made clear[5].

In the present paper, to compare the stabilities of aerosols depending on the nature of the added vapors as on well as their concentrations and to inquire into the role of the vapors in stabilizing the aerosols, the rate of coagulation in the presence of such vapors was observed by means of the ultramicroscopic method, using three kinds of aerosol, i.e., the fogs of aqueous ammonium chloride solution, glycerol and dioctyl phthalate (D.O.P.).

Experimental

The apparatus used for the present work consists of the following parts—an air-driving train, an aerosol generator, a vaporizer for the admixture, a smoke chamber and an ultramicroscope. The functions of these parts are mentioned successively.

The aerosols were prepared by two methods.

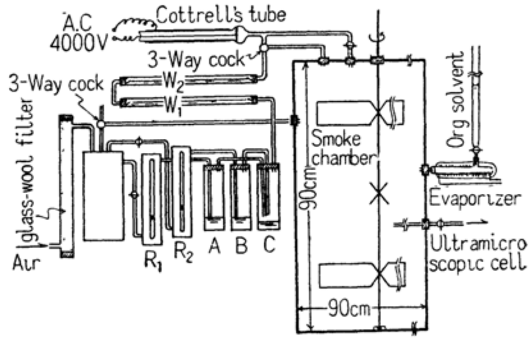

Fig. 1. Preparative system of the fog of aqueous NH_4Cl solution and other constructions.

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[1] R. Whytlaw-Gray and H. S. Patterson, "Smoke", Edward Arnold and Co., London, 1932, Chapter 5 and 6.

[2] Y. Fujitani, *J. Chem. Soc. Japan, Pure Chem. Section*, **74**, 661 (1953).

[3] Ibid., **73**, 817 (1952); **75** 89 (1954).

[4] Ref. 1., P. 184.; "Handbook on aerosols", The Uuited Stated Atomic Energy Commission, Washington, DC., 1950, p. 65.

[5] Y. Fujitani, *J. Chem. Soc. Japan, Pure Chem. Section*, **73**, 817 (1952), **74**, 704 (1953).

a) **The fog of aqueous ammonium chloride solution.**—The fog of aqueous ammonium chloride solution was obtained by almost the same way as used in the previous experiments[5], and its modified generating system is indicated in Fig. 1. In this figure, A and B are 9.6 N hydrochloric acid and 11.2 N aqueous ammonia washing bottles, respectively, each containing 100 c.c. of the reagent, and bubbling velocity of clear air coming from a compressor through a glass wool filter and being regulated by the rota-meters, R_1 and R_2, is 0.7 l./min. for the former, and 0.3 l./min. for the latter, respectively. The gases of hydrogen chloride and ammonia driven from these bottles were mixed in the reaction chamber, C, where ammonium chloride smoke was produced. During the passage of the ammonium chloride smoke over a water surface in two glass tubes, W_1 and W_2, (each 2.0 cm. in inside diameter and 60 cm. long), ammonium chloride particles were changed to the fog droplets of aqueous ammonium chloride solution because of a strong tendency of ammonium chloride particle to absorb water vapor[6]. At the same time, the excess gas, chiefly ammonia gas, is absorbed through the water surface. Therefore, water in these two tubes, W_1 and W_2, was renewed in each run for obtaining a good reproducibility in fog preparation.

The concentration of ammonium chloride in the fog particle was found to be about 20 % by weight as an average which was determined by collecting the droplets of fog through a Cottrell's precipitator and analyzing them chemically by means of Mohr's method, a maximum deviation being less than 3 % by weight. Table I shows the mass concentrations and average radii of aqueous ammonium chloride droplets. Average radii shown in the table were determined from the droplet sizedistribution curve obtained by measuring the settling velocity of each fog droplet in an ultramicroscopic cell. The number of fog droplets observed is about 300 for one size-distribution curve. The size-distribution curve is depicted in Fig. 2. It can be seen from Fig. 2 and Table I that the reproducibility is very good.

TABLE I

AVERAGE RADII AND MASS-CONCENTRATIONS OF THE FOG OF AQUEOUS NH_4Cl SOLUTION OBSERVED UNDER THE SAME EXPERIMENTAL CONDITIONS

No. of expt.	Average radii (μ)	No. of expt.	Mass concentration (mg./l.)
1	0.24	2	17.9
3	0.20	4	18.1
5	0.24	6	18.3
7	0.23	8	17.9
9	0.21	10	17.4
Mean	0.22	Mean	17.9

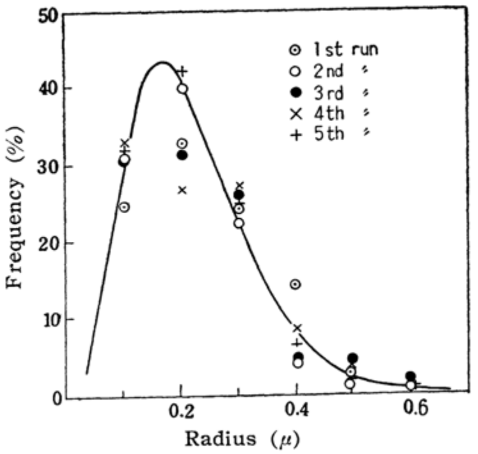

Fig. 2. Size-distribution curve of the fog of aqueous NH_4Cl solution obtained by the measurement of settling velocity of droplets.

b) **The fogs of glycerol and D. O. P.**—The fogs of glycerol and D.O.P. were prepared by an all-glassed L-type generator[7], which was the modified LaMer-Sinclair's monodisperse aerosol generator[8], consisting of three parts—boiler, reheater and condensation tube. The generator is illustrated in Fig. 3. The boiler (horizontal part, 3.5 cm. inside diameter, 20 cm. long) in which liquids or solids to be dispersed were placed, and the reheater (vertical part, 3.5 cm. inside diameter, 18 cm. long) were both electrically heated at the desired temperatures with a nicrom-jacket through variable voltstats. These two temperatures were measured by thermometers, T_1 and T_2, respectively. The condensation tube was a double-wall glass tube, and its inner tube is 2.0 cm. in inside diameter and 25 cm. long.

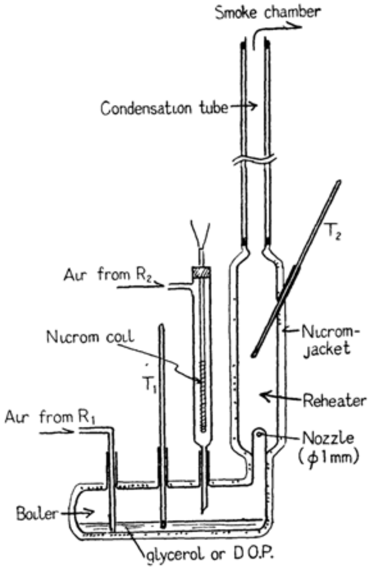

Fig. 3. L-type aerosol generator.

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[6] S. Twomey, *J. Applied Phys.*, **24**, 1099 (1953).

[7] To be published for detailed description.

[8] V. K. LaMer and D. Sinclair, *Chem. Rev.*, **44**, 245 (1949).

In order to obtain a good monodisperse fog by this generator, the temperatures must be kept properly for each material and the condensation nuclei added in a proper amount. Nuclei were supplied by an electrically heated nicromwire which was coiled along a quartz tube 8 cm. long.

The amount of glycerol or D.O.P. put in the boiler is 30 c.c.. The vapor driven from the boiler by bubbling air and the air laden nuclei were completely mixed in the reheater through two nozzles of 1 mm. diameter. The flow velocities of vapor and nuclei are both 0.5 l./min.. The mixture of vapor and nuclei was passed through a condensation tube where slow cooling and subsequent condensation of vapor on nuclei occurred.

The fogs produced were so nearly monodisperse that higher order Tyndall spectra[8] were visible. The temperatures both in the boiler and the reheater under the above mentioned preparative procedure and the average radii obtained under these conditions are as shown in Table II for glycerol and D.O.P.. Average radii were determined from the measurements of settling velocity in the same manner as mentioned above.

TABLE II

TEMPERATURES OF PREPARATIVE CONDITIONS AND AVERAGE RADIUS OF DROPLET

Substances	Temperature of generator (°C) Boiler	Reheater	Average radius (μ)
Glycerol	135	145	0.18
D.O.P.	160	180	0.22

The fogs produced by these procedures, a) and b), were re-dispersed homogeneously by stirring for 5 min. in a smoke chamber which is a wooden octagonal box coated with paraffin, 90 cm. in height, its content being 700 l.. The initial particle concentration in the smoke chamber was maintained at 2 to 5×10^5 per c.c. through out the whole experiment.

Organic liquid to be tested for its stabilizing action was evaporated into the smoke chamber from a vaporizer which was made of a quartz tube, 2.0 cm. in inside diameter and 20 cm. long, having a side tube connected to a burette. The organic liquid was poured into the vaporizer from the burette. The vaporizer was electrically heated by a nicrom-jacket. The concentration of organic vapor in the smoke chamber, expressed in m. mol./l., was calculated from the burette reading. The mixture of fog and organic vapor was stirred homogeneously for 5 min. as in the case of the fog alone.

The organic liquids used were carefully purified by the usual procedure and their boiling points were found to coincide fairly well with those of the literature[9],

The number of particles per unit volume is counted by an ultramicroscopic technique. The volume of visible field in the ultramicroscopic cell was 1×10^{-6} c.c.. The brilliant points appearing in the dark field were counted and summed up for a fog droplet driven successively into the ultramicroscopic cell. The counting of fog droplets is done every 3 to 5 min. for an interval of 60 to 120 min.. The magnification of ultramicroscope was ×80.

All experimentals were carried out at room temperature, 16 to 19°C..

Results

The decrease in number of fog droplets determined ultramicroscopically is shown in Fig. 4, 5 and 6 as the typical examples.

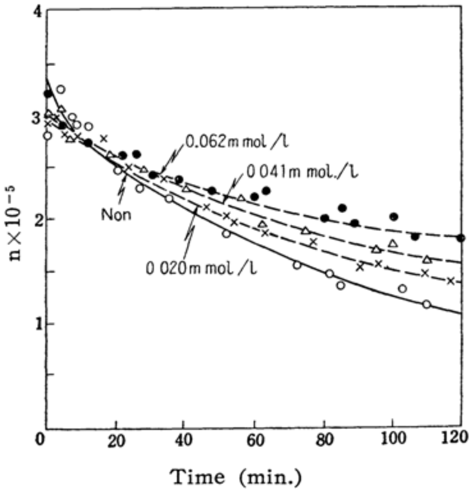

Fig. 4. Variation of droplet number per c.c. as a function of time and concentration of ethyl acetate mixed to the fog of aqueous NH_4Cl solution.

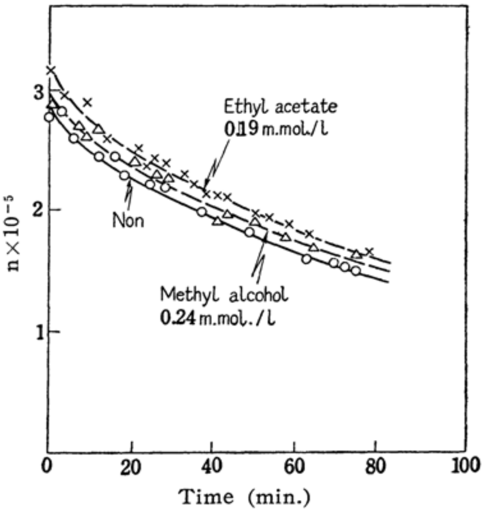

Fig. 5. Variation of droplet number per c.c. as a function of time and some vapors mixed to the fog of glycerol.

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[9] A. Weissberger et. al., "Organic Solvents…Physical Properties and Methods of Purification", 1955.

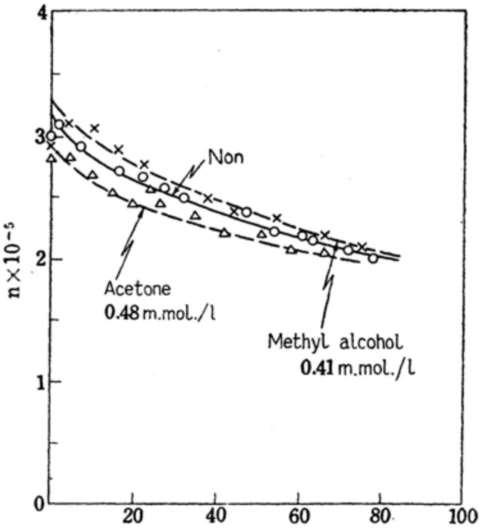

Fig. 6. Variation of droplet number per c. c. as a function of time and some vapors mixed to the fog of D.O.P..

In these figures, solid curves represent a decrease in number of fog droplets for a fog system without organic vapor, and broken curves refer to one with organic vapor. All curves showed a tendency to decrease monotonously in the course of aging.

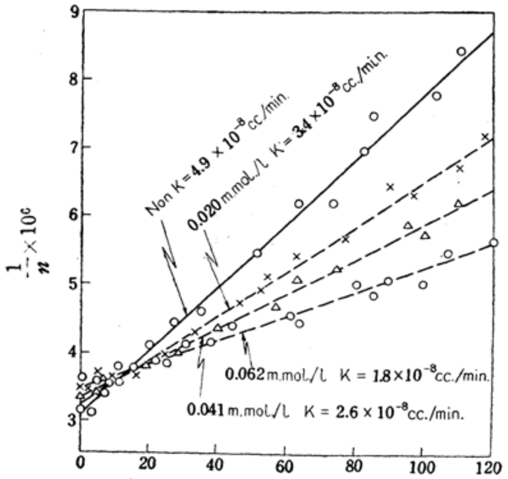

Fig. 7. Linear relationship between reciprocal number of droplet and time obtained as an influence of ethyl acetate concentration mixed to the fog of NH_4Cl-aqueous solution. *K* is a coagulation constant calculated from the slop of observed line.

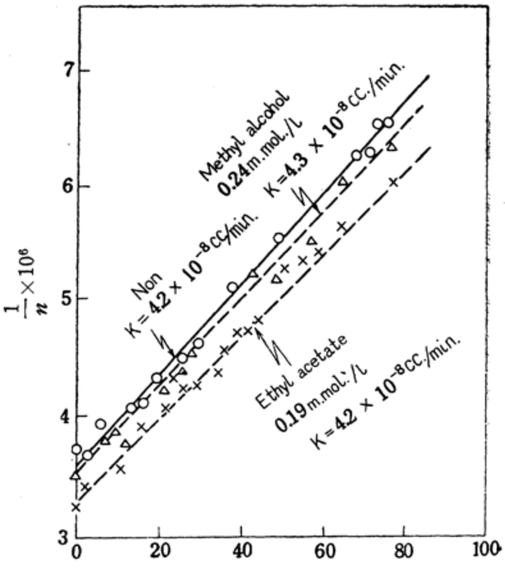

Fig. 8. Linear relationship between reciprocal number of droplet and time obtained as an influence of some vapor mixed to the fog of glycerol.

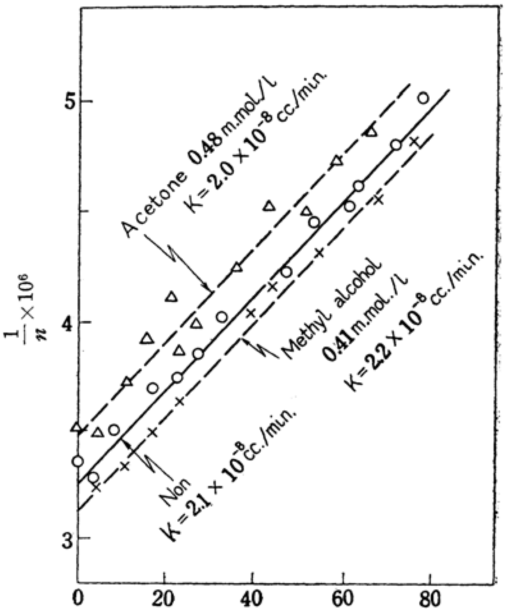

Fig. 9. Linear relationship between reciprocal number of droplet and time obtained as an influence of some vapors mixed to the fog of D.O.P..

Converting these droplet number—time graphs into a reciprocal droplet number—time ones, the linear relationships are obtained for all of them as in Figs. 7, 8 and 9. The linear relationship holds throughout all the runs of experiment. It may be noticed readily that the slope of line varies markedly with the nature and the concentration of the vapor added to the fog of aqueous ammonium chloride solution, while, in contrast with this, it remains almost unaltered in the case of the fogs of glycerol and D.O.P. even in a greater concentration.

Smoluchowski's equation is expressed as follows,

$$1/n-1/n_0=Kt, \qquad (1)$$

or in a more correct form,

$$1/n-1/n_0=K'(1+A\lambda/r)t \qquad (2)$$

where n_0 and n are the numbers of droplets per unit volume at the begining, $t=t_0$, and time t, respectively, K and K' are the coagulation constants equal to $4kT/3\eta$ (k: Boltzman's constant, η: viscosity of air) numerical value being 1.8×10^{-8} c.c./min. in air at $T=293$°K, λ the mean free path of air molecules, r the radius of fog droplet, and A a constant having a value of 0.7 to 1.7. $A\lambda/r$ in equation (2) gives a correction term arising from a slipage between a fog droplet and air molecules during the movement of a fog droplet in still air; therefore, the smaller the value r becomes, the greater becomes the value $A\lambda/r$.

Thus, the slopes obtained experimentally are equal to K. However, K might be used instead of K', for the comparison of relative stabilizing effects of organic vapors on the same aerosol since the droplet size-distribution curve was practically unchanged for the fogs used in all runs.

The dependence of coagulation constant, K or K', upon the concentration of various organic vapors mixed are plotted in Figs. 10 and 11 for the fogs of aqueous ammonium chloride solution, glycerol and D.O.P..

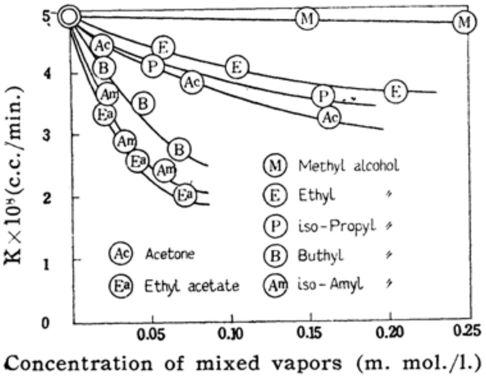

Fig. 10. Variation of the coagulation constant, K, with the concentration of mixed vapors for the aqueous NH_4Cl solution fog. Symbol ◎ is the average coagulation constant for a pure fog and its value is 4.9×10^{-8} c.c./min..

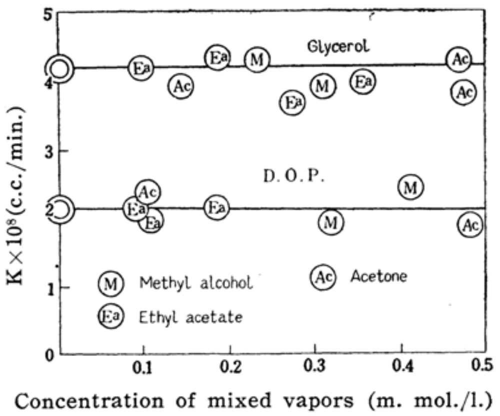

Fig. 11. Variation of the coagulation constant as a concentration of mixed vapors for the fogs of glycerol and D.O.P.. Symbols ◎ are the coagulation constant for the pure fog of glycerol and D.O.P. and their values are 4.2×10^{-8}c.c./min. and 2.1×10^{-8}c.c./min., respectively.

From these figures, it is found that for the same vapor the more it is added, the more strongly the fog of aqueous ammonium chloride solution is stabilized, but no effect is observed for the other fogs within the limit of experimental precision. For the former, the coagulation constant falls off to nearly one-third under the most stabilized condition.

Discussion

Although a number of studies have been made by Russian workers and others since 1930 concerning the effects of admixture[10], the information obtained is not always in agreement with one another, because the experimental conditions and procedures were not unified. Especially, the defect of a criterion for the ability of stabilization must be noticed.

The stability of aerosol should be governed by the internal stability[11], expressed in terms of the particle concentration and the particle size-distribution, both of which are determined a priori by the condition of formation, provided that the collision efficiency has a constant value in all of the collision processes. Therefore if the collision efficiency of aerosol particles may be altered as suggested by Patterson[12] either by the

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[10] T. Tatibana, *J. Chem Soc. Japan, Pure Chem. Sec.* **68**, 53 (1947); I. S. Artemov, *J. Phys. Chem., (U. S. S. R.)*, **20**, 533 (1946); I. V. Petryanov et al., ibid., **15**, 811 (1941); etc.

[11] D. Sinclair, "Air Pollution", Chapter 18, p. 169, McGrow-Hill Book Co., 1952.

[12] Ref. 1., Chapter 16.

TABLE

EFFECT OF VAPORS ON THE INCREASE OF CHARGED

Fog	Sign of elec. charge	Vapor concn. $\left(\frac{\text{m.mol.}}{\text{l.}}\right)$	Percentage of charged droplet for various time in the aging time (min.)					
			0	10	20	30	40	60
Aqueous NH_4Cl solution	+	Non	9.1	9.9	14.0	14.2	15.5	19.6
	−		8.8	11.0	11.3	16.0	14.9	19.2
Glycerol	+	Non	6.5	7.9	9.5	14.5	12.8	18.8
	−		8.1	12.2	13.2	15.4	22.1	27.0
D.O.P.	+	Non	14.0	17.1	19.6	27.0	28.2	37.3
	−		13.7	14.8	17.3	20.2	23.9	27.6

physico-chemical structure of surface or by the changes in surface state, we may have a most important problem which has been disregarded up to date. This will be developed from now on. To study this in an orthodox way, it is better to evaluate the coagulation constants experimentally for various fogs to which vapors are added, and to compare them with one another.

From this point of view, the experimental results obtained above are interesting by reason of a large difference among the values of the coagulation constant for the fog of aqueous ammonium chloride solution and the degree of lowering of these values which are parallel with a concentration of mixed vapors. The tendency of a stabilizing effect of mixed vapor agrees with the Traube's rule[13] referring to the surface activity of the homologous series of organic compounds on pure water surface. These facts are considered to be valuable as the fundamental basis in discussing the stabilities of aerosols. It may be inferred that the coalescence of droplets in the collision process is obstructed by a decrease in surface tension somewhat in an analogous manner as the stabilization of emulsion system pointed out by Donnan[14]. Because these organic vapors have not shown capillary activity when mixed with the fogs of glycerol and D.O.P..

In a strict sense of the discussion concerning the effects of admixtures, it appears that many other factors should be taken into account with equal weight. These may be classified chiefly into four factors i.e., i) the changes in density and viscosity of medium, ii) the growth of droplets by the condensation of admixtures[15], iii) the change in distribution in electric charge of fog droplets, iv), particularly, in the case of the aqueous ammonium chloride solution, the disappearance of fog droplets by evaporation of water, etc..

First, the effects of i) and ii) have a relation to the mobility of fog droplets by the Brownian movement and sedimentation under the gravity during standing in a still medium. However, these influences caused by the change of physico-chemical properties of the medium may be small.

Second, the growth of a fog droplet by the condensation of vapor may depend upon its partition ratio between the vapor and the droplet phase, but the concentration of vapor in all experimental conditions is too low to make a droplet grow larger. In fact, no appreciable changes of fog droplet size were ascertained by ultramicroscopic observation.

Third, the change in the proportion of a charged droplet was similar irrespective of the presence of vapor during the aging. The results obtained from the electrophoresis of charged droplets in an electric field of an ultramicroscopic cell are shown in Table III. The contribution of an electric charge on the coalescence process has been also proved to be small[16].

Finally, it is generally accepted that a dissipation of aqueous aerosol by evaporation is very rapid, but, in the present case, the fog droplets consist of an aqueous ammonium chloride solution which is so concentrated that the fog system is very stable.

If the contribution of these factors is not small, it must result in a change in the coagulation constant for the fogs of glycerol and D.O.P.. Therefore, these effects are all negligible in the present work as clearly seen from the afore-said experimental results.

Most of the discussion has gone no

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[13] I. Traube, *Ann.* **265**, 27 (1891).

[14] Donnan, *Z. physik. Chem.*, **31**, 42 (1899).

[15] V. K. LaMer and R. Gruen, *Trans. Faraday Soc.*, **48**, 410 (1952); V. K. LaMer and S. Coston, *Science*, **118**, 516 (1953).

[16] W. B. Kunkel, *J. Applied Phys.*, **19**, 1053 (1948).

III

DROPLET PERCENTAGE DURING THE AGING

Increase rate of charged droplet (%/min.)	Vapor concn. (m.mol. / l.)	Percentage of charged droplet for various times aging time (min.)						Increase rate of charged droplet (%/min.)
		0	10	20	30	40	60	
0.17	0.24 Acetone	9.9	10.3	13.5	16.2	16.2	20.1	0.17
0.17		9.4	12.7	14.4	15.0	17.1	21.9	0.19
0.22	0.42 Acetone	6.1	9.4	11.2	10.2	16.1	19.1	0.20
0.31		9.0	10.2	15.3	18.4	19.5	27.3	0.32
0.37	0.39 Ethyl acetate	15.1	20.0	23.4	25.0	28.3	39.5	0.37
0.23		11.2	14.6	18.4	17.3	23.2	27.5	0.20

further than establishing a few general quantitative remarks, but there is a reason to believe that the mechanism of stabilizing action of the organic vapors on the fog system is largely attributable to a capillarity of admixtures. In order to prove that this conclusion is of general applicability, we need further studies, both theoretical and experimental, to be pursued as the more fundamental problems.

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