Coagulation of Lead Chloride Aerosol in the Presence of Water Vapor

Polydisperse submicronic lead chloride aerosols were generated from melt phase under dry and humid conditions. The particle size and concentration increased with increasing generation temperature. The aerosol particles generated in a dry atmosphere were spherical while the aerosol particles generated in humid atmosphere showed development of crystallinity at the surface.

Coagulation rates of the aerosol generated in a dry atmosphere were measured at room temperature under different humidities. The coagulation rates were in good agreement with Smoluchowski's theory, modified to include the effect of polydispersity and were unaffected by humidity. The interaction of lead chloride particles with the water vapor was characterized by a process of adsorption at the interface. The coagulated aerosol exhibited a chain structure for humidities lower than 70% and, at higher humidities, compact agglomeration was observed.

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SCOPE

Submicronic lead halide aerosols are present in automobile exhaust. Air pollution by these aerosols is of great concern to air pollution engineers and gasoline manufacturers due to its effect on human health and agriculture. The concentration and the particle size of these aerosols determine the severity of the effect. Due to the process of coagulation and settling, the concentration and particle size is time dependent. No experimental information is available on the lead chloride aerosol regarding the coagulation.

In this study the effect of temperature and humidity on the aerosol generation was assessed. The coagulation rates of lead chloride aerosol were determined experimentally under the various humidity conditions which may be expected in the atmosphere. Electron microscopy was used to examine the coagulated aerosol.

CONCLUSIONS AND SIGNIFICANCE

The polydisperse submicronic lead chloride aerosol was generated in dry and humid conditions. The particle size distributions of the aerosol generated under the two conditions were found to be the same. This particle size distribution was characterized by a log probability function having a geometric number mean diameter of 0.05 μ and a geometric standard deviation of 2. The number concentration of the aerosol ranged from 10^6-10^8 particles/cm^3. The aerosol generated in humid atmosphere showed development of crystallinity at the surface.

The aerosol generated under dry condition was used in a 60-liter chamber for the coagulation study. The concentration 'n' $\left(\frac{\text{No. particle}}{\text{cm}^3}\right)$ of aerosol followed a straight line on 1/n vs. time graph for several hours. The settling of aerosol and the change in coagulation rate became significant in the latter period. The coagulation constant was in good agreement with the value calculated from the theory for monodispersed aerosol taking into consideration the effect of polydispersity. No effect of humidity on the coagulation rates was observed in the range 0 to 95% R.H.

Electron micrographs of the coagulated aerosol showed chain-like growth for experiments carried out under humidity below 70% R.H. At and above 70% R.H. a more compact agglomerate structure was observed, indicating adsorption of water on the particles.

THEORETICAL CONSIDERATIONS

All particles in an aerosol cloud are in constant motion due to Brownian, convective, and gravitational forces. When two particles come into contact with each other during their motion, they can adhere and then act as a single entity. This process occurs throughout the cloud and is called the coagulation of the aerosol.

The extent of coagulation is dependent on the probability of collisions between the particles. Their Brownian motion is a random process and the probability of the collisions is dependent on the mean particle velocity. This is a function of the particle size and it increases as the

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size of the particle decreases.

Convection due to thermal or hydrodynamic forces also causes a relative motion of the particles which contributes to coagulation.

In gravitational field the larger particles settle faster than the smaller ones, and during settling they come into contact with them contributing to coagulation.

The loss of particles due to deposition by Brownian motion and settling may significantly affect the progress of coagulation in a laboratory sized chamber and must be accounted for.

Brownian Coagulation of Aerosol

The simplest form of the theory was developed by Smoluchowski and is discussed by Fuchs (1964). Considering the aerosol to be monodisperse and the coagulation to occur by Brownian motion alone, he derived the following equation for the rate of decrease of particle number concentration:

$$\frac{dn}{dt} = - K_0 n^2 \qquad (1)$$

A useful form of this equation is obtained by integration of Equation (1)

$$\frac{1}{n} - \frac{1}{n_0} = K_0 t \qquad (2)$$

where n (#/cm^3) is the number concentration at time t, n_0 is number concentration at time $t = 0$, and K_0 is the coagulation constant. The value of K_0 can be estimated theoretically for monodisperse aerosol by the formula

$$K_0 = \frac{4\,\kappa T}{3\,\eta} \times (1 + 0.864\, l/r) \Big/ \left(1 + 0.75 \frac{l_b}{r}\right) \qquad (3)$$

where T is the absolute temperature. The term $(1 + 0.864\, l/r)$ represents the Cunningham correction for particles having radius comparable to the mean free path of gaseous medium 'l'. The term $(1 + 0.75\, l_b/r)$ represents the noncontinuum correction according to Fuchs (1964). 'l_b' is the mean free path of the aerosol particles.

Equation (2) indicates that a plot of $1/n$ versus t is a straight line with a slope $= K_0$.

It has been established by experiments that this straight line relationship holds till the concentration drops to quite a low value (one thirtieth of the initial) for monodispersed aerosols.

For polydispersed aerosols, the Smoluchowski theory holds within experimental error, at least in the initial stages. The value of K_0 is usually higher than predicted by Equation (3) due to the polydispersity. Exact solution to the problem of coagulation of a polydisperse aerosol is complicated. The coagulation constant for two particles of unequal sizes depends on the sizes of the individual particles. The possibility of collisions between particles of all the sizes over the entire size distribution has to be considered. This usually requires lengthy computer calculations.

The experimental data on coagulation show that the $1/n$ versus time plot is represented by a straight line. This suggests the possibility of using an average coagulation constant K for the coagulation of a polydisperse aerosol instead of K_0 in Equation (2). Fuchs (1964) and more recently Pich (1972) have derived expressions for the ratio of the average coagulation constant K to the value of K_0 calculated from Equation (3) and based on the arithmetic average radius $\overline{r}$,

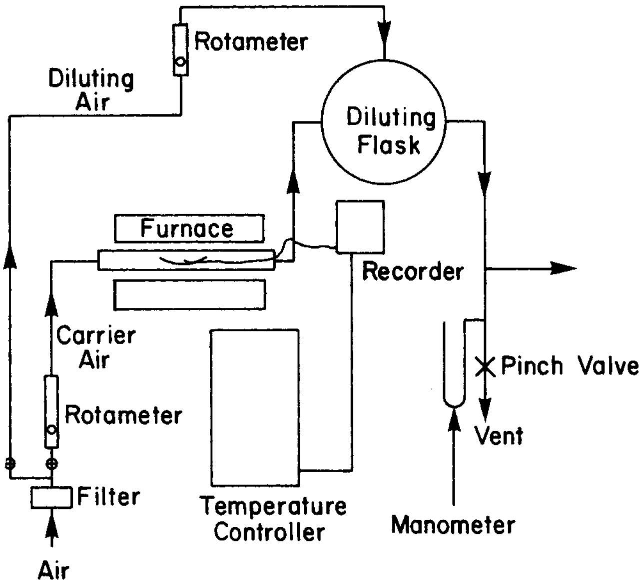


Fig. 1. PbCl$_2$ aerosol generator.

$$\psi = \frac{K}{K_0}(r) = \frac{1 + \overline{r}\left(\overline{\frac{1}{r}}\right) + Al\left(\overline{\frac{1}{r}}\right) + Al\,\overline{r}\left(\overline{\frac{1}{r^2}}\right)}{2\left(1 + Al\frac{1}{\overline{r}}\right)} \qquad (4)$$

ψ is called the polydispersity factor, and

$$r^{\overline{K}} = \int_0^\infty r^k f(r)\, dr$$

Coagulation in Presence of Deposition

The concentration of an aerosol enclosed in a chamber falls with time as a result of the Brownian deposition on the walls of the chamber. For this study a cylindrical chamber was used. The loss of particles due to Brownian motion to the chamber wall was assessed.

The loss of particles to the walls of a finite cylinder with its height equal to or greater than its diameter is intermediate to the loss for the case of infinitely long cylinder and that for a sphere of the same radius. From the appropriate solutions for these two limiting cases (2) the extent of deposition due to Brownian motion was found to be negligible during the experiment.

The fall in concentration of aerosol particles of diameter a due to settling under gravity is given by Fuchs (1964)

$$\ln n(a) = \ln n_0(a) - \frac{V_s(a)t}{H} \qquad (5)$$

where H is the height of the chamber. The arithmetic average diameter was used to calculate the loss of particles in the chamber used in the present study. Equation (5) predicts a 10% particle loss in five hours. Due to convection the actual loss is expected to be less than that predicted.

A simple model was used by Gillespie and Langstroth (1951) who used a coefficient β to take into account the loss due to deposition and settling in the following manner:

$$\frac{dn}{dt} = - (K\, n^2 + \beta n) \qquad (6)$$

where β is a constant which includes deposition to the walls and the bottom of the chamber.

In the integrated form Equation (6) becomes

$$\ln\left(\frac{1}{n}+\frac{K}{\beta}\right)=\ln\left(\frac{1}{n_0}+\frac{K}{\beta}\right)+\beta t \tag{7}$$

Rewriting Equation (6),

$$\frac{d(\Phi)}{dt}=\frac{d\left(\frac{1}{n}\right)}{dt}=K+\beta\Phi \tag{8}$$

which is the slope of the $1/n$ versus t curve at a given time. At time $t = 0$, the initial slope of the $1/n$ versus t curve is thus

$$\left.\frac{d\left(\frac{1}{n}\right)}{dt}\right|_{t=0}=K+\beta\Phi_0 \tag{9}$$

The relative importance of the deposition is represented by the term $\beta\Phi$. The term Φ increases with time, increasing the importance of the deposition. When the term $\beta\Phi_0$ is small compared to the value of K, the value of the coagulation coefficient K can be calculated by the initial slope of the $1/n$ versus t curve. Recently Ahn and Gentry (1972) have presented a computer solution for the coagulation equation considering the loss of particles due to settling. The effect of deposition increases as the coagulation proceeds.

EXPERIMENTAL WORK

Aerosol Generation

The generator for the lead chloride aerosol is based on the vaporization condensation principle. As shown schematically in Figure 1, lead chloride is maintained at a constant temperature in a combustion boat in a furnace. A stream of dry filtered air is passed over the combustion boat. The air picks up lead chloride vapor. The air-vapor mixture cools after leaving the furnace, and condensation of the vapor takes place to form aerosol particles. The aerosol is then diluted by mixing it with a stream of dry filtered air in the dilution flask.

Table 1. Size Characteristics of Aerosol as a Function of Generation Temperature

Temp., °C	GNMD, μ	σ_g	GMMD, μ
420	0.03	1.8	0.085
450	0.042	1.79	0.116
505	0.05	2.00	0.211
520	0.059	1.70	0.137

$\ln(\text{GMMD}) = \ln(\text{GNMD}) + 3.0 \ln^2 \sigma_g$.
$\log_{10}(\text{GMMD}) = \log_{10}(\text{GNMD}) + 6.909 \log^2_{10} \sigma_g$.

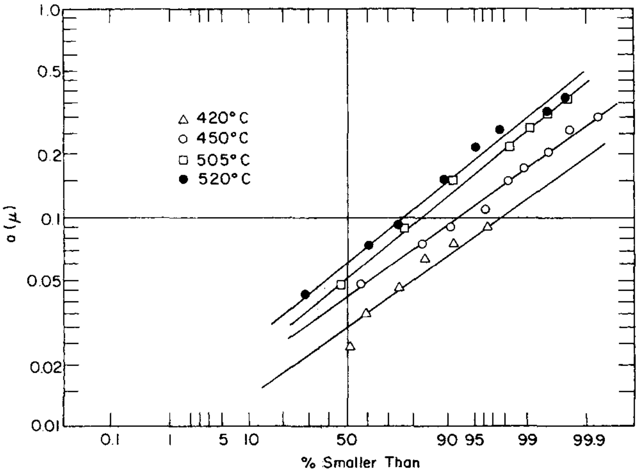


Fig. 2. Size distributions of $PbCl_2$ aerosols generated at various temperatures.

An air flow rate of 20 liters/min. was used. The generation temperatures were comparable to automobile engine temperatures. The aerosol was generated at 420°, 450°, 505°, and 520°C. After diluting the aerosol with 16 liter/min. of air, the aerosol was collected on carbon coated grids in a M.S.A.® electrostatic precipitator.

The size distribution of the particles was determined by counting and sizing the particles from enlarged electron micrographs covering various viewing fields of the sample. The cumulative percentage for different sizes was plotted on log-probability paper (Figure 2). The straight line behavior indicates that the size distribution can be represented by log-normal distribution function.

The log-normal distribution function by count is described by the following formula:

$$f(a)=\frac{1}{a\sqrt{2\pi}\ln\sigma_g}\exp-\frac{\ln^2\left(\frac{a}{a_n}\right)}{2\ln^2\sigma_g} \tag{10}$$

where a_n is the geometric number mean diameter (GNMD) and σ_g is the geometric standard deviation: a measure of the polydispersity or breadth of the size distribution.

The values of the GNMD and GMMD (on mass basis) and σ_g are summarized in Table 1.

Effect of Generation Temperature on Particle Characteristics

At the lowest temperature (420°C) the mean particle size was 0.03μ. A few aggregates of considerably larger size ($\approx$0.5μ) were observed. The aerosol particles generated at 450° and 505° were of increasingly larger size, and again very few aggregates were present. At the highest temperature (520°) the particles were larger still, but now a considerable number of aggregates were present as the concentration was very high.

Based on these observations, a temperature of 505°C was chosen for the aerosol coagulation study since it resulted in both the desired size range of the aerosol and the absence of aggregates.

Effect of the Humidity of the Primary Air on Particle Characteristics

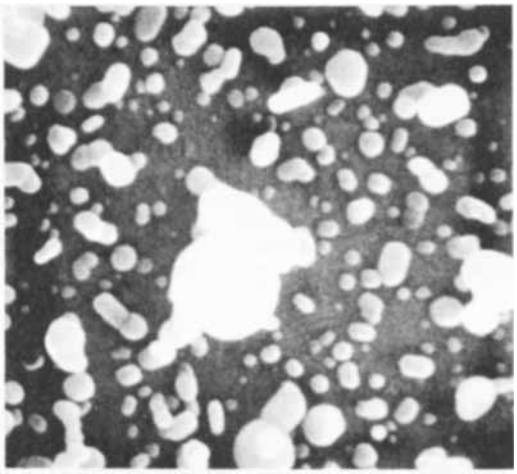
The effect of moisture in the air on the particle characteristics was studied by comparison of the aerosol generated in dry and humid air. In the first case, a dry stream of air was used (R.H. < 10% at 26°C).

In the latter case the primary air was bubbled through water maintained at 80°F before passing it through the generator (R.H. = 88% at 26°C).

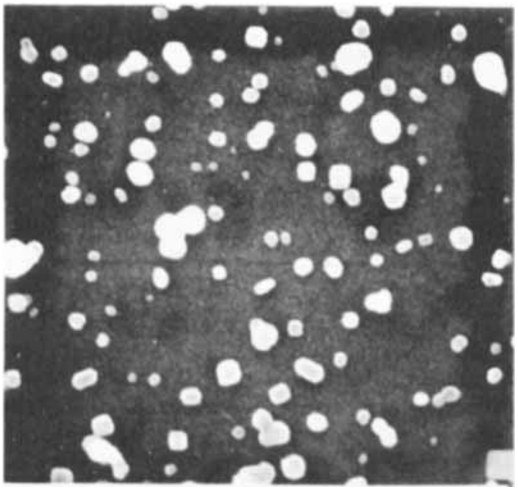
The aerosol was collected on an aluminum foil in the M.S.A.® electrostatic precipitator and the samples were examined in a scanning electron microscope. Figures 3a and 3b show the aerosol particles at 30,000 X magnification. The particles generated in humid air (3a) showed crystallinity at the edges and were cubic in nature. The particles generated under dry conditions (3b) were less crystalline in appearance, and a considerable proportion showed an elongated nature representing the orthorhombic crystal structure of $PbCl_2$. A possible change of crystal structure at the surface was indicated by these observations.

Aerosol Coagulation

A schematic drawing of the experimental set-up is shown in Figure 4. The coagulation experiments were carried out in the aerosol chamber. For the present experiments the dry aerosol was used. The aerosol chamber was a 15-in. I.D. plexiglass cylinder of 2 cft. volume. In this chamber the lead chloride aerosol was exposed to various conditions of humidity. The chamber was humidified by passing air of controlled humidity through the chamber until the inlet and outlet humidities (measured by an electronic hygrometer) were equal. A thermistor probe was used to measure the temperature inside



(a), Dry Air (R.H. < 10% at 80°F); 30,000X



(b), Humid Air (R.H. = 88% at 80°F); 30,000X

Fig. 3. Scanning electron micrographs of aerosol generated in dry and humid air.

the chamber. The chamber was provided with an inlet port for the aerosol. Six ports were provided for sampling the contents of the chamber at various levels. A 3/8-in. O.D. sample tube or a thermistor was inserted at various radial positions through each of the six ports. Sampling errors due to wall effect and inhomogeneity in the chamber were minimized by experimentally determining the most suitable sampling location. An absolute filter was fitted to the top of the chamber and a vacuum pump was connected to a port at the bottom of the chamber. The condensation nuclei counter was connected to the sample probe positioned at the center of the chamber. Other sample probes were inserted at radially central positions to withdraw samples for a thermal precipitator and light scattering photometer.

A condensation nuclei counter ("Small-Particle Detector Type CN," made by Gardner Associates, Schenectady, N. Y.) was used to measure the number concentration of the aerosol. The counter measured the concentration of particles above 1.5 × 10^{-7} cm in radius. The sample volume was of the order of 100 cm^3. The lowest concentration detectable was 200 nuclei/cm^3 and concentrations as high as 10^7 nuclei/cm^3 could be measured.

A Strong-Ficklen thermal precipitator was used to collect aerosol sample on electron microscope grids.

At the beginning of each experiment, the chamber was first cleaned by drawing filtered air through it by means of a vacuum pump. When there were no nuclei present, the vacuum pump was turned off. (The minimum nuclei concentration detectable by the condensation nuclei counter (CNC) was 200 nuclei/cm^3). Aerosol was generated at 505°C and vented till the flow was stabilized. The aerosol was then introduced through a port (1 cm. in diameter), into the chamber for 10 to 15 seconds. The relative humidity in the chamber changed slightly due to the aerosol stream and this lower value was taken as the relative humidity for a particular run. The concentration of the aerosol was immediately measured with the condensation nuclei counter. Readings by various instruments were then taken at desired intervals to study the coagulation rate. The volume of the aerosol removed for sampling was made up by room air sucked through the absolute filter. This dilution of the aerosol in the chamber was insignificant.

In some of the experimental runs, the extent of deposition was determined by lining the walls with plastic wraps. These wraps were cooked in 1% HNO_3 and the amount of lead was determined by atomic absorption spectroscopy.

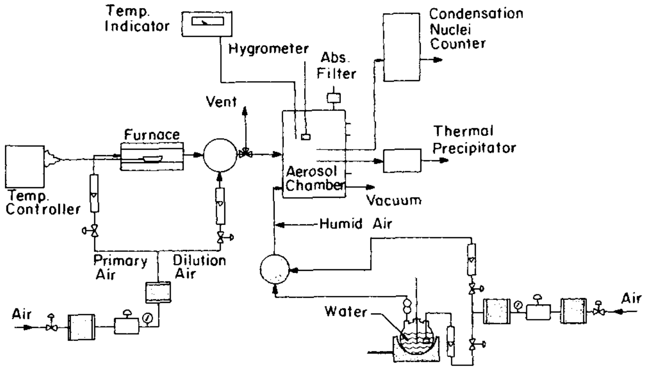


Fig. 4. Apparatus for coagulation studies.

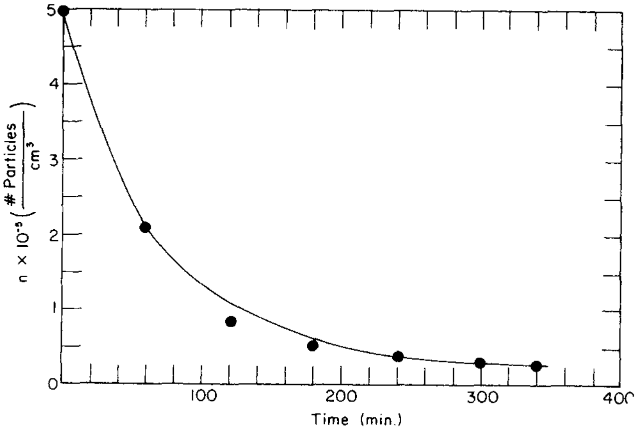


Fig. 5. *n* vs. time for run 1.

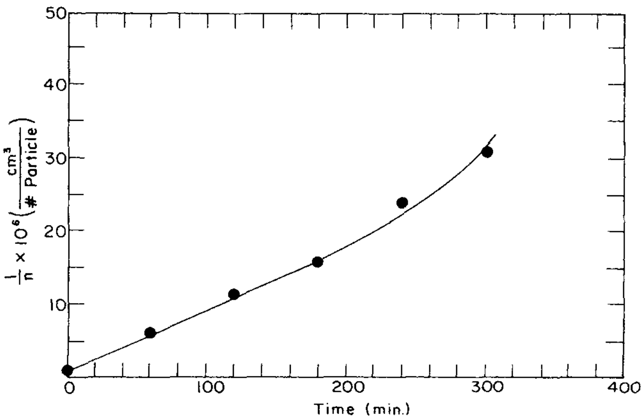


Fig. 6. $\frac{1}{n}$ vs. time for run 2.

TABLE 2. SUMMARY OF COAGULATION DATA

$K_{\text{Theoretical}} = 1.4 \times 10^{-9}$ cm³/s

Run no.	R.H. %	Coagulation const. K(cm³/s)	Deposition
1	2	1.35×10^{-9}	
2	2	1.32×10^{-9}	
3	2	1.22×10^{-9}	3% by weight
4	34	1.50×10^{-9}	
5	60	1.55×10^{-9}	3% by weight
6	69	1.37×10^{-9}	3% by weight
7	73	1.33×10^{-9}	
8	76	1.22×10^{-9}	
9	85	1.31×10^{-9}	
10	95	1.29×10^{-9}	
Average		1.35×10^{-9}	

RESULTS OF COAGULATION EXPERIMENTS

The results of the coagulation experiments are presented in Table 2. Typical change in the number concentration as a function of time is shown in Figure 5. In Figure 6 the same data is plotted in terms of inverse concentration ($1/n$) as a function of time. The straight line behavior in the initial stages indicates that the coagulation of lead chloride particles follows Smoluchowski's theory according to equation (2). The significance of the deposition is reflected in the curvature appearing after 2 to 2-½ hours.

The value of the coagulation constant was determined from the initial slope of the $1/n$ versus t plot. The value is in good agreement with the theoretical value. The theoretical value of the coagulation constant K_0 calculated by Equation (3) for $\overline{r} = 0.032\ \mu$ was 0.78×10^{-9} cm³/s. The polydispersity factor calculated by Equation (4) was found to be 1.77. The theoretical estimate of the average coagulation constant K is 1.4×10^{-9} cm³/s.

No effect of the relative humidity of the air on the coagulation constant was observed. This is not unexpected since the deviation of the coagulation constant (max. + 17%) is probably due to variation in mean particle size and distribution. For example, a 20% change in mean particle size ($a_n = 0.04$ instead of 0.05) can cause + 18% increase in the coagulation constant.

For runs numbers 5 and 6, the extent of deposition was determined from the plastic lining by atomic absorption. Significant deposition was found only on the bottom and contributed about 3% of the total aerosol by weight.

Substituting the values of the theoretical coagulation constant and the values of β calculated from the experimental deposition loss (3% loss, $\beta \approx 1 \times 10^{-6}\ \text{s}^{-1}$) into Equation (9) when n is 10^6 #/cm³

$$\left.\frac{d\,(1/n)}{dt}\right|_{t=0} = 1.4 \times 10^{-9} + 5 \times 10^{-6} \times \frac{1}{10^6}$$

$$= 1.4 \times 10^{-9} + 1 \times 10^{-12}$$

Therefore, the error in calculating the coagulation constant from the $1/n$ versus t curve is

$$\frac{1 \times 10^{-12}}{1.4 \times 10^{-9}} \times 100 = 0.07\%$$

This illustrates the validity of the coagulation constant obtained from the experimental data. The contribution due to deposition becomes increasingly important as the time progresses, as shown by the $1/n$ versus t curves.

The aerosol coagulated under dry atmosphere was collected on an e.m. grid in a thermal precipitator. Figure 7a shows the original aerosol. Figure 7b shows the aerosol collected after 2 hours. Figure 7c shows the aerosol collected during the entire run on an e.m. grid at the bottom of the chamber. The aggregates show a chain structure with branching occurring at larger particles.

The formation of linear aggregates has been observed in smoke and fumes by many workers. Fuchs (2) has summarized the various conditions under which linear growth occurs. Presence of external electrical or magnetic fields or free bipolar charge on the particles results in stringy aggregates.

Electron micrographs of the aerosol aggregate under the different humidity conditions are shown in Figure 8. The chain growth of aggregated particles was observed for experiments with relative humidity from 0 to 60%. At 69% R. H., the aggregate had more random characteristics. Some fusion at the interparticulate boundaries was also observed under a scanning electron microscope. Scanning electron micrographs were also taken for aerosols from runs numbers 2, 6, and 10 are shown in Figure 9. At 95% relative humidity, the condensation on the particle surface is distinctly evident. The condensation has resulted in partial dissolution of the particles.

CONCLUSIONS

The coagulation rates of lead chloride aerosol having initial number mean size of 0.05 μ were measured under air humidities ranging from almost dry to saturated conditions. The air humidity was found to have no effect on the

(a) Fresh Aerosol
5000X

(b) Thermal Precipitor
Sample After 1 Hr
5000X

(c) Deposit on Bottom
During Entire Run
5000X

Fig. 7. Electron micrographs of coagulating aerosol for run 1.

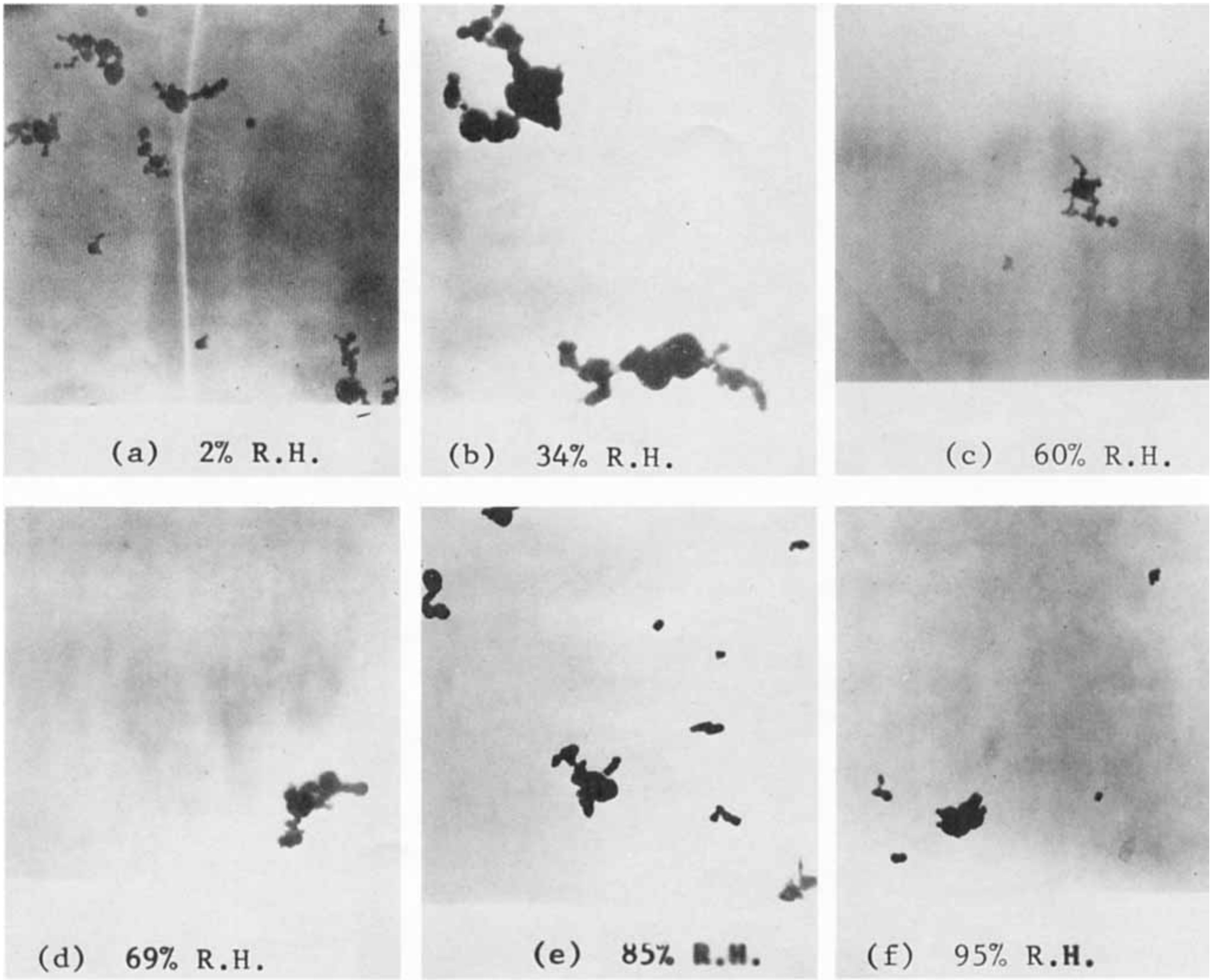

(a) 2% R.H. (b) 34% R.H. (c) 60% R.H. (d) 69% R.H. (e) 85% R.H. (f) 95% R.H.

Fig. 8. Electron micrographs of aerosol coagulated at various humidities.

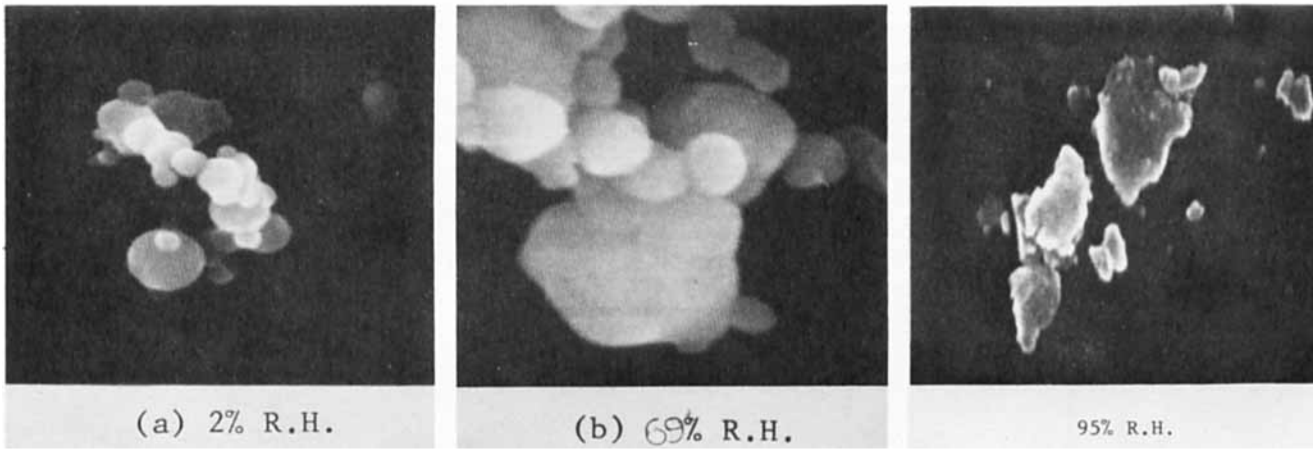

(a) 2% R.H. (b) 69% R.H. 95% R.H.

Fig. 9. Scanning electron micrographs of aerosol coagulated at various humidities.

coagulation constant. Above air humidity of 70%, presence of liquid water film was observed. The water film did not increase the size of the primary droplets significantly to affect the rate of loss of the particles.

The agglomerate resulting from coagulation under air humidities up to 69% exhibited a chain growth. At higher humidities compact round growth was observed. Presence of water film on the particle surface and interstices was also evident.

The coagulation of the polydisperse lead chloride aerosol is controlled by Brownian motion. The Smoluchowski theory for the monodisperse aerosol could be used to correlate the rate of loss of particles in the initial 2 to 2-½ hours. The coagulation constant calculated from the average initial particle size was in good agreement with the experimental data.

The extent of deposition during the experiment was determined and was insignificant in the calculation of the coagulation constant.

The effect of polydispersity on the coagulation constant was found to be in good agreement with the theoretical prediction.

ACKNOWLEDGMENT

This work was performed under a multi-sponsored industrial research program at IIT Research Institute. The contents of this paper are derived from the doctoral thesis of M. B. Ranade.

NOTATION

a = diameter of the particle
a_n = geometric number mean diameter, GNMD
a_m = geometric mass mean diameter, GMMD
A = constant in the Cunningham correction (0.864)
d = differential symbol
$f(a)$ = frequency of size distribution
l = mean free path of gas molecules
l_b = mean free path of aerosol particles
n = number concentration, no. particles/cm^3
n_0 = number concentration at time $t = 0$
$n(a)$ = number concentration of particles of diameter a
N = total number of particles in the aerosol cloud
r = radius of the particle
V_s = settling velocity, cm/s

Greek Letters

β = deposition loss constant, no. particles/s
η = viscosity of the gaseous medium, poise
κ = Boltzmann constant 1.38×10^{-16} ergs/°K
μ = linear dimension (microns), 10^{-4} cm
σ_g = geometric standard deviation
Φ = inverse number concentration $(1/n)$, cm^3/no. particles
ψ = polydispersity factor

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Diffusion in Synthetic Faujasite Powder and Pellets

Transient sorption rates of allene and methylacetylene in synthetic faujasite (Linde 13X) powder and self-bonded pellets are studied in a constant-volume, constant-pressure system at three temperatures. The intracrystalline diffusion coefficients are found to be in the order of 10^{-11} cm^2/s and the activation energy for diffusion is 4.0 kcal/g-mole.

A simple bipore distribution model for transient diffusion in macropores and micropores is presented. It agrees well with the experimental data and quantitatively predicts the macropore diffusion coefficients. The flow in the macropores is found to be in the Knudsen flow regime.

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The phenomena of diffusion in porous pellets become quite complicated when zeolites are used as the pellets because they contain both a micropore structure within the crystals (intracrystalline diffusion) and a macropore structure between crystals (intercrystalline diffusion). Quantitative prediction of the individual diffusion coefficients can be of importance in interpreting the experimental data and improving engineering design in such important operations as purification of gas streams, separation processes, and catalytic conversion units.

Previous work on the study of diffusion in zeolites concentrates mostly in intracrystalline diffusion with powder materials. Recent studies on the diffusion in solids with a bipore distribution include the theoretical analysis by Furusawa and Smith (1973), both theoretical and experimental investigation on diffusion in ion exchanged resins by Ruckenstein et al. (1971), and the experimental study by Sargent and Whitford (1971) using commercial 5A molecular sieve pellets. The present work employed a constant-pressure constant-volume technique to examine quantitatively some of the effects of micropore and macropore structure on the determination of the diffusion coefficient. Diffusion coefficients were evaluated based on a mathematical model taking into account intercrystalline and intracrystalline diffusion and adsorption. Equilibrium adsorption isotherms and rates of sorption of allene and methylacetylene were measured on synthetic faujasite (13X) powder. Diffusion measurements were also made with 13X pellets formed from the material used in the powder experiments. No binder was added, thus eliminating the possible complication which it might cause.