

A New Hypothesis for the Mechanism of Ice Nucleation on Wetted AgI and AgI•AgCl Particulate Aerosols

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(Manuscript received 23 April 2001, in final form 25 February 2003)

ABSTRACT

A potential molecular mechanism of ice nucleation on AgI and AgI • AgCl particulates involves rearrangement of ordered water molecule clusters associated with hydrated Ag⁺ ion patches. This nucleation mechanism is thought to occur rapidly at -5° to -20°C on substrate particles wetted by water. This hypothesis is based on analysis of the rates of ice crystal formation and ice nucleus activities observed in experiments previously conducted in a 1-m³ isothermal cloud chamber using chemical kinetics. These experiments examined the chemistry of wetted AgI colloid particles involving electric charge separations between the particles and adjacent solution. The rate of nucleation is slowed by the presence of alkali and alkaline earth halides in concentrations greater than approximately 10^{-3} M in the water wetting the particles. Match of the crystal structure of the substrate with that of the ice may have no effect on this mechanism.

1. Introduction

As explained in Frost and Pearson (1953), a mechanism is a model of detailed processes devised to explain facts gained from kinetic measurements and other experiments. Other models may result from consideration of additional facts or from a new concept of the structure of matter.

The mechanism of nucleation described in this article is a process of transformation of matter at the molecular level, leading to formation of viable ice embryos on wetted, submicron, AgI particles. The postulated mechanism explains results previously obtained in a series of cloud chamber experiments. These experiments addressed heterogeneously nucleated ice crystal formation rates, multistep mechanisms of crystal formation, and ice nucleus activity. Ice nucleus activity is defined as the number of ice crystals obtained per gram of AgI nucleant aerosol under specified conditions of temperature and cloud water content. To a considerable extent, the explanation for this nucleation mechanism also relies on knowledge gained from extensive studies on AgI colloids conducted at the Department of Colloid and Physical Chemistry, Agricultural University, Wageningen, Netherlands.

In chemistry, two separate approaches have been used in studies of heterogeneous nucleation of the solid phase from vapor, melt, or solution. The first treats the het-

erogeneous substrate as a surface that lowers the energy of activation, thus inducing nucleation of the solid phase. This follows a theoretical thermodynamic approach. The second approach treats the substrate as a catalyst, which speeds up the rate of nucleation to the point where it becomes measurable. Data on the rates of product formation and how the rates vary with parameter changes (e.g., composition, temperature, concentration) are used to deduce the fundamental nucleation mechanism. This approach, experimental chemical kinetics, has been used in this study.

We hypothesize that our ice nucleation mechanism occurs on wetted AgI and AgI • AgCl particles at temperatures of -5°C and lower. In the previously conducted experiments, various alkali halides were cogenerated with AgI or AgI • AgCl (e.g., Feng and Finnegan 1989). Hygroscopic composite aerosol particles were either injected into a cloud chamber after dilution with dry air or subjected to a transient supersaturation with respect to liquid water. The latter was achieved by diluting the aerosol sample with saturated ambient temperature air before injection into the cloud chamber. Parent AgI and AgI • AgCl aerosols also were studied under transient supersaturation conditions to force wetting of aerosol particles.

Silver iodide particles adsorb water onto hydrophilic sites (Birstein 1955; Zettlemyer et al. 1961; Tcheurekdjian et al. 1964; Corrin and Barchet 1970) and, when wetted as colloids, form hydrated surfaces (de Keizer and Lyklema 1981). The term *wetted particle* is used to mean that bulk liquid water is present on the particle surface. A *hydrated surface* has one or two layers of

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water molecules on a particle surface. If the particle is charged, the water molecules may have a different orientation than they would have on an uncharged particle. This last point is key in the development of our hypothesis.

This paper is structured as follows: section 2 presents the history of prior laboratory studies that generated the observations from which our hypothesis is drawn; section 3 reviews fundamental physicochemical features of AgI surface chemistry; section 4 critically reviews results of several chemical systems, providing context for development of the hypothesis; and section 5 fully states and develops this new hypothesis.

2. Prior laboratory studies

Silver iodide–sodium iodide ($2\text{AgI} \cdot \text{NaI}$) composite aerosols (Vonnegut 1950) have been used in cloud seeding programs for more than 50 years. Silver iodide–potassium iodide ($2\text{AgI} \cdot \text{KI}$) composite aerosol was used in Project White Top, a cloud seeding program in Missouri, from 1960 to 1964 (Braham and Flueck 1970). It was not until 1979, however, that studies on the rates and mechanisms of ice crystal formation were initiated using these and other nuclei in the isothermal cloud chamber of the Cloud Simulation and Aerosol Chamber facility at Colorado State University.

In this series of studies, rates and mechanisms of ice crystal formation were established for AgI and AgI • AgCl (DeMott et al. 1983); $2\text{AgI} \cdot \text{NaI}$ (Blumenstein et al. 1987); $2\text{AgI} \cdot \text{KI}$ (Rilling et al. 1984); AgI • AgCl • x NaCl (Feng and Finnegan 1989); and AgI • AgCl • 0.125 KCl, NaCl, LiCl, and MgCl_2 (Finnegan 1998). In the AgI • AgCl nucleus study, the ratio of AgI to AgCl was varied from greater than 9:1 to 4:1. For the AgI • AgCl • x NaCl nuclei, x was varied from 0.5 to 5.

The mechanism of ice crystal formation for parent AgI and AgI • AgCl nuclei at water saturation in a supercooled cloud was shown to involve, as the slowest or rate-determining step, contact of water droplets by nucleus particles (DeMott et al. 1983). The rate of ice crystal formation grew with an increase in cloud droplet concentration. Initial condensation of water vapor onto composite nuclei (e.g., $2\text{AgI} \cdot \text{NaI}$ or AgI • AgCl • x NaCl) was followed by freezing and crystal growth. In this case, the rate of ice crystal formation was independent of cloud droplet concentration. The rate-determining step for composite nuclei was not identified. Although the molecular mechanism of ice phase nucleation was not determined in any of these studies, the extensive collection of data on ice crystal formation rates, together with the corresponding ice nucleus activity data, provide information needed for determination of the molecular nucleation mechanism.

Aerosols of AgI • AgCl have superior ice nucleus activity compared to those of AgI at water saturation in a supercooled cloud (DeMott et al. 1983). Both AgI and AgI • AgCl aerosols nucleate the ice phase rapidly when

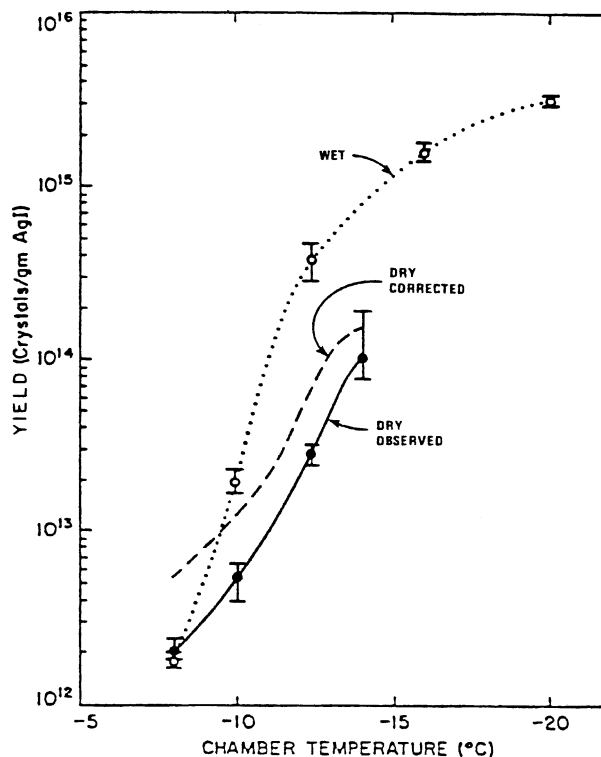


FIG. 1. Observed ice nucleus activity (solid line) of $2\text{AgI} \cdot \text{NaI}$ nuclei for the dry injection experiment as a function of temperature. Chamber liquid water content was 0.5 g m^{-3} . The dashed line is the same data corrected for airflow dilution. The dotted line is the observed ice nucleus activity for the moist air injection experiment. Airflow corrections were not required because nucleation proceeded to completion in less than 2 min. (From Blumenstein et al. 1987.)

subjected to transient supersaturation with respect to liquid water in a supercooled cloud (DeMott 1995; Finnegan and Pitter 1988). Ice nucleus activities at -10°C , however, do not increase substantially. In all these experiments, results were achieved by injecting a 4-L syringe of saturated, room-temperature air containing the nucleus aerosol into the cloud chamber at the supercooled test temperature.

The $2\text{AgI} \cdot \text{NaI}$ nucleus aerosol characterization study (Blumenstein et al. 1987) showed a poor ice nucleus activity spectrum and slow rate of ice crystal formation at water saturation in a supercooled cloud compared to results for AgI • AgCl • NaCl aerosols. No satisfactory explanation was found for this behavior at the time. A hypothesis to explain the low activity was that sodium iodide combines with AgI, increasing solubility of the compound in water. No explanation was offered at the time for the slow rates of ice crystal formation. When subjected to a transient supersaturation, the rate of ice crystal formation increased substantially and activity at -8° and -10°C increased to the values of the parent AgI nucleus, as shown in Fig. 1.

In a study by Rilling et al. (1984), a poor ice nucleus activity spectrum and very slow rates of ice crystal for-

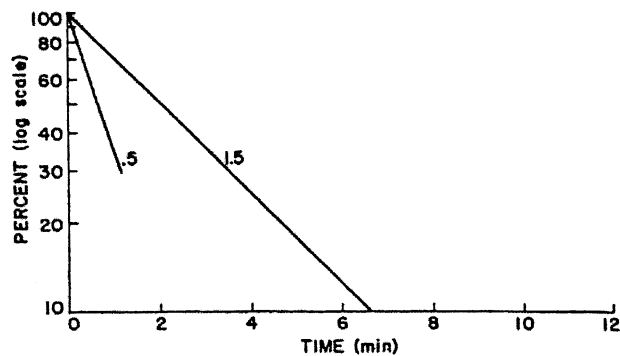


FIG. 2. Percent depletion of $2\text{AgI} \cdot \text{KI}$ ice nuclei that react to form ice crystals. Chamber temperature was -10°C with two liquid water contents, 0.5 and 1.5 g m^{-3} . Both tests done with partial moist dilution. (From Rilling et al. 1984.)

mation also were found for the $2\text{AgI} \cdot \text{KI}$ composite aerosol when it was tested at water saturation in a supercooled cloud. In this experiment the rate of ice crystal formation increased when the nuclei were subjected to transient supersaturations, and activities increased in a manner similar to that observed for $2\text{AgI} \cdot \text{NaI}$ composite aerosols. It was noted that the rate of ice crystal formation under transient supersaturation conditions was faster when the isothermal cloud chamber droplet concentration was 2100 cm^{-3} (with liquid water content of 0.5 g m^{-3}) than when the condensation was 4250 cm^{-3} (with liquid water content of 1.5 g m^{-3}) (Fig. 2). This results from the chamber droplet population competing for available supersaturation; the supersaturation excess is more quickly depleted as the plume of humid aerosol mixes with the surrounding cloud with higher droplet concentration, thereby limiting growth of the water droplets nucleating on the $2\text{AgI} \cdot \text{KI}$ particles and leading to higher solute concentration. This result suggests that salt concentration is a factor in the nucleation rate.

Study of the $\text{AgI} \cdot \text{AgCl} \cdot \text{NaCl}$ nucleus aerosols (Feng and Finnegan 1989) was initiated to find a condensation-freezing nucleus aerosol with rates of ice crystal formation and an activity spectrum superior to those of $2\text{AgI} \cdot \text{NaI}$ and $2\text{AgI} \cdot \text{KI}$ aerosols. New acetone solution combustion formulations were devised to generate $\text{AgI} \cdot \text{AgCl} \cdot x \text{ NaCl}$ aerosols (where x ranged from 0.5 to 5) on the assumption that removing the solubilizing characteristics of NaI would permit higher $\text{AgI} \cdot \text{AgCl}$ ice nucleus activity to be realized. Substitution of NaCl for NaI and KI was anticipated to increase rates of ice crystal formation. While increasing the ratio of NaI and KI to AgI beyond the $2\text{AgI} \cdot \text{NaI}$ and KI formulas severely degrades ice nucleus activity, it was anticipated that the NaCl formulas might reach their optimum activity at a different ratio. This proved to be the case; both the activity and rate of ice crystal formation increased at -10°C as x was increased from 0.5 to 4. The $\text{AgI} \cdot \text{AgCl} \cdot 4 \text{ NaCl}$ nucleus showed the highest activity and fastest rate of ice crystal formation at

water saturation. Activity decreased at $x = 5$, but the rate continued to increase. These results are shown in Figs. 3 and 4.

The behavior of these nucleus aerosols was hypothesized to be due to the Kelvin effect. Due to surface tension, smaller droplets require higher supersaturation to grow through condensation of water vapor. Assuming that AgI particle size distribution remained the same, increasing the ratio of NaCl to AgI would result in larger droplets. Larger droplets have lower surface tensions and grow relatively faster at lower supersaturations by vapor condensation resulting in decreased salt concentrations. This is additional evidence that high salt concentrations in solution on the nucleating particle hinder the ice nucleation process.

Rates of ice crystal formation increased dramatically when $\text{AgI} \cdot \text{AgCl} \cdot x \text{ NaCl}$ aerosols were subjected to transient supersaturations on injection into supercooled cloud. This was true at all temperatures from -6° to -20°C (Feng and Finnegan 1989). In contrast to the behavior of parent AgI and $\text{AgI} \cdot \text{AgCl}$ aerosols, which did not show increased activities at -10°C under these conditions, the $\text{AgI} \cdot \text{AgCl} \cdot 4 \text{ NaCl}$ aerosol reached 10^{15} ice crystals per gram, a fivefold increase over that obtained with the $\text{AgI} \cdot \text{AgCl}$ aerosols.

Further studies on new ice nucleus compositions (Finnegan 1998) indicated that the activities and rates of ice crystal formation of $\text{AgI} \cdot \text{AgCl}$ nuclei at water saturation were a function of the cation for a series of composite nucleus aerosols of the general composition $\text{AgI} \cdot \text{AgCl} \cdot 0.125 X$, where X was KCl , NaCl , LiCl , or 0.0625 MgCl_2 . An $\text{AgI} \cdot \text{AgCl} \cdot 0.125 \text{ KCl}$ composite aerosol showed the fastest rate and highest activity at -10°C and water saturation; the equivalent NaCl composite showed a lower rate and activity; and the LiCl composite showed a much lower rate and activity. The $\text{AgI} \cdot \text{AgCl} \cdot 0.125 \text{ MgCl}_2$ composite gave a very low rate and activity, but an $\text{AgI} \cdot \text{AgCl} \cdot 0.0625 \text{ MgCl}_2$ aerosol gave more usable results for comparison with the KCl , NaCl , and LiCl composites. When subjected to transient supersaturations with respect to liquid water, all of the compositions functioned rapidly and with increased activity. The $\text{AgI} \cdot \text{AgCl} \cdot 0.0625 \text{ MgCl}_2$ aerosol still showed residual effects at a slightly slower rate. Rate results are shown in Figs. 5 and 6. The ice crystal formation rate was measured experimentally, but the ice nuclei concentration depletion rate was plotted in Figs. 5 and 6, as has been done in prior publications (DeMott et al. 1983). It is apparent from these figures that alkali and alkaline earth cations have a role in the ice formation process beyond hygroscopicity.

3. Silver iodide colloid chemistry

An explanation for the diverse behaviors of AgI and $\text{AgI} \cdot \text{AgCl}$ nucleus aerosols cogenerated with alkali and alkaline earth halides can be found in the extensive literature on AgI colloids and suspensions. Excellent re-

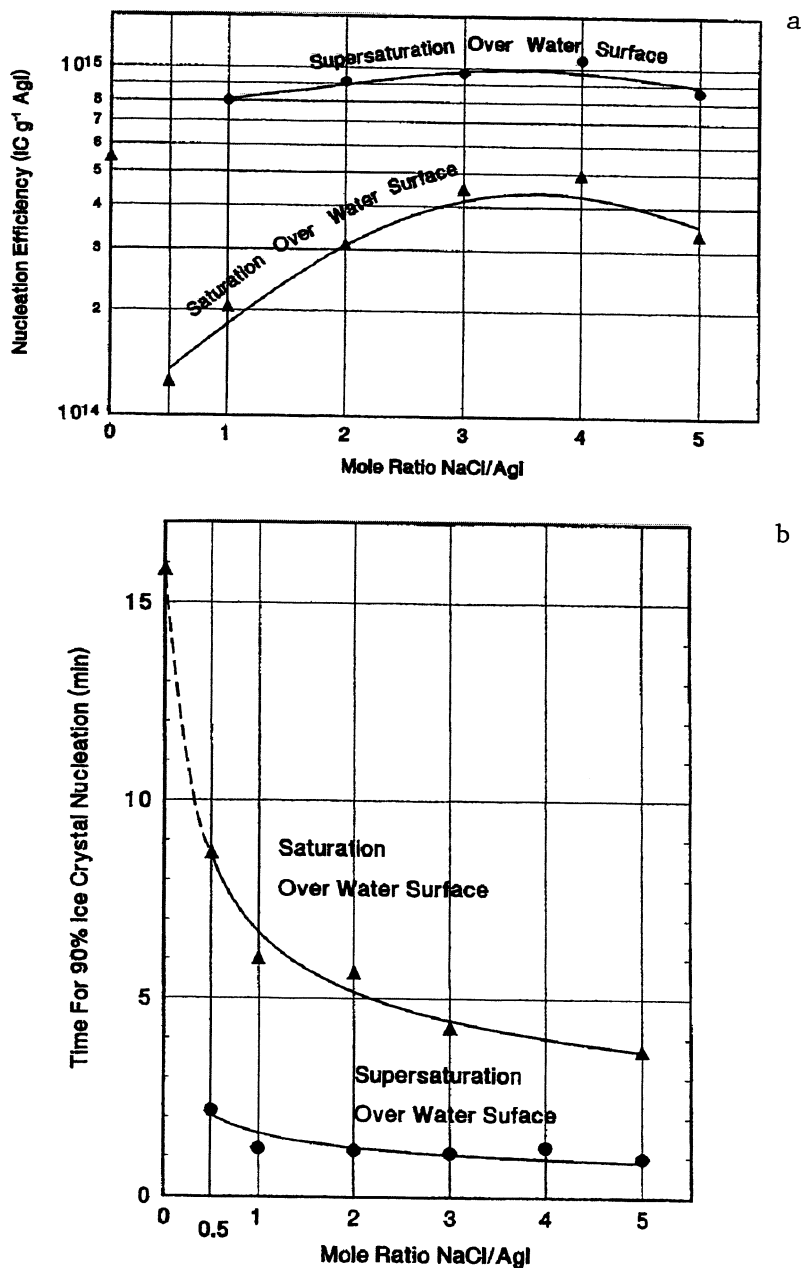


FIG. 3. (a) Nucleation efficiencies of $\text{AgI} \cdot \text{AgCl} \cdot x \text{NaCl}$ nucleus aerosols and (b) times for 90% ice crystal nucleation as a function of the NaCl/AgI ratios at -10°C . (From Feng and Finnegan 1989.)

views of the subject can be found in van Leeuwen and Lyklema (1986) and Bijsterbosch and Lyklema (1978). The most notable studies of silver iodide colloids and suspensions have been completed by the Laboratory for Physical and Colloid Chemistry, Agricultural University, Wageningen, Netherlands.

Because they are easily prepared, easily purified, relatively insoluble, and relatively nonreactive chemically, silver iodide colloids are known as model colloids (Bijsterbosch 1986; Lyklema 1977). Due to the mobility

of the Ag^+ cation in the AgI matrix (Remez and Chebotin 1984), AgI electrodes can be used to investigate the electrochemistry of their colloid systems.

When pure, AgI has solubility in cold water of $3 \times 10^{-6} \text{ g L}^{-1}$. This solubility appears to increase in the presence of inert electrolytes (e.g., NaCl, KCl; Vincent and Lyklema 1970). An inert electrolyte is a soluble, ionizable salt that in solution furnishes neither a potential determining ion (Ag^+ or I^-) nor any ion that would be specifically adsorbed by the colloid particle. Silver

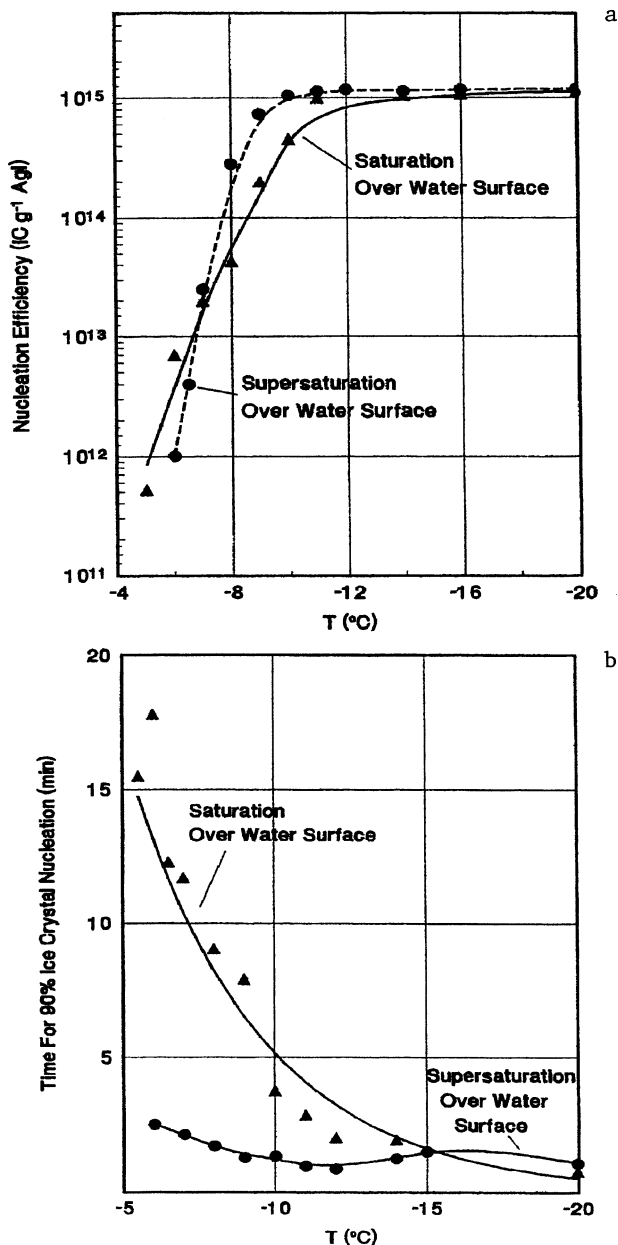


FIG. 4. (a) Nucleation efficiencies and (b) times for 90% ice crystal nucleation of $\text{AgI} \cdot \text{AgCl} \cdot 4 \text{NaCl}$ composite nuclei as functions of temperature and humidity. (From Feng and Finnegan 1989.)

iodide colloid particles are in dynamic equilibrium with AgI in solution, which is completely ionized. The solubility product (the product of the concentrations of Ag^+ and I^- ions in gram ionic weights per liter of solution) of the dissolved AgI is approximately 10^{-14} in the system at equilibrium. Hydrated Ag^+ and I^- ions adsorb and desorb from discrete separate patches on the AgI particle surface (de Keizer and Lyklema 1981), forming a hydration or water layer.

Pure silver iodide colloid particles are negatively charged. Silver and iodide ions are the potential deter-

mining ions, and the addition of one or the other (e.g., as AgNO_3 or NaI to the colloid solution) will shift the negative charge on the particles either toward or away from the position of zero charge (PZC). The addition of sufficient AgNO_3 can change the charge on the particles from negative to positive. A diffuse electrical double layer surrounds each colloid particle in the absence of added salts. The addition of other soluble and ionizable salts (termed supporting electrolytes) at concentrations greater than about 10^{-3} M will change the electrical double layer from diffuse to compact. Structural features called the inner and outer Helmholtz layers are formed in the compact layer and have a total thickness of about 5 Å. Cations of the supporting electrolyte (called counter ions) are attracted to the compact electrical double layer when the particles are negatively charged. These counter ions form the Stern layer adjacent to the surface of the particles (Fig. 7). Cations in the Stern layer screen and slow the rate of adsorption and desorption of hydrated Ag^+ ions onto particles surfaces.

4. Analysis

a. $2\text{AgI} \cdot \text{NaI}$ and $2\text{AgI} \cdot \text{KI}$ nucleus aerosols

At water saturation, we attribute low rates of ice crystal formation of $2\text{AgI} \cdot \text{NaI}$ and $2\text{AgI} \cdot \text{KI}$ nucleus aerosols to high concentrations of I^- ions; a potential determining ion, in the solution droplets formed on the AgI particles after injection of the aerosol into the cloud chamber. The excess of I^- ions results in an increase of hydrated I^- ions attachment to the AgI particles in order to maintain solubility product concentration at 10^{-14} . This greatly increases particle negative charge. This increase and resulting high electric charge on the particle promote an orienting effect on the water dipoles that opposes any water "structuring" in the water hydration layer. This orienting effect on water molecules at high negative charge is called "structure breaking" in colloid chemistry, while water-structuring formation at lower negativities is called "structure forming" (Vincent and Lyklema 1970). We hypothesize that the orienting effect breaks the hydrogen bonding structure in the hydration layer around the particles and that this slows the ice nucleation process. High NaI or KI supporting electrolyte concentration ensures that the electric double layer is compact around the AgI particles, and high Na^+ or K^+ concentration in the Stern layer would screen the adsorption-desorption process of Ag^+ cation hydrates on and off particle surfaces, thus slowing the nucleation rate.

Subjecting these nuclei to transient supersaturations in the cloud chamber increases the rate of ice crystal formation by diluting the alkali halide concentration in the solution droplets below 10^{-3} M. Dilution changes the electric double layer from compact to diffuse. The

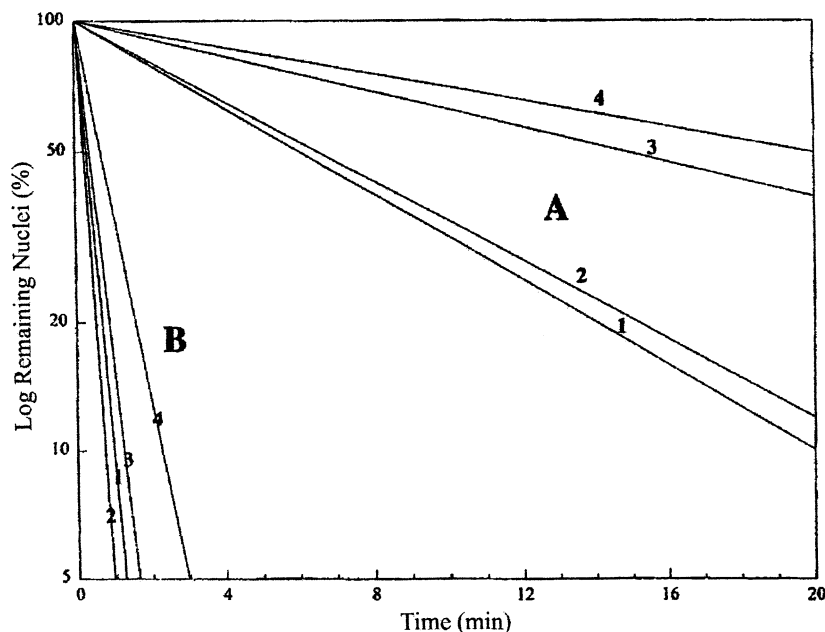


FIG. 5. Rates of depletion of ice nuclei concentration at -10°C in a $1 - \text{m}^3$ cloud chamber with a 1.5 g m^{-3} liquid water content cloud (4250 cloud droplets cm^{-3}). Nucleus aerosols tested include 1) $\text{AgI} \cdot \text{AgCl} \cdot 0.125\text{KCl}$, 2) $\text{AgI} \cdot \text{AgCl} \cdot 0.125 \text{ NaCl}$, 3) $\text{AgI} \cdot \text{AgCl} \cdot 0.125 \text{ LiCl}$, and 4) $\text{AgI} \cdot \text{AgCl} \cdot 0.0625 \text{ MgCl}_2$. Group A is nucleus aerosols injected into the chamber after diluted with -40°C dewpoint air. Group B is nucleus aerosols injected after diluted with saturated air to induce a transient supersaturation. The rate for 1 in group B is also the rate measured for $\text{AgI} \cdot \text{AgCl}$ hydrophobic nucleus aerosol, injected after dilution with saturated air. (From Finnegan 1998.)

nucleation rate can then increase in the absence of cationic screening.

The decrease in ice nucleus activity of $2\text{AgI} \cdot \text{NaI}$ and $2\text{AgI} \cdot \text{KI}$ aerosols compared to AgI aerosol and $\text{AgI} \cdot \text{AgCl} \cdot \text{NaCl}$ composite aerosols must be due to the solubilizing properties of the two alkali iodides. After a final dilution with saturated room-temperature air, injecting $2\text{AgI} \cdot \text{NaI}$ aerosol into the cloud chamber results in a substantial increase in ice nucleus activity compared to that achieved with dry injection, for temperatures of -10°C and lower (see Fig. 1). This suggests that smaller-sized particles dissolve in higher NaI or KI concentration solutions formed at water saturation (the Kelvin effect). When transient supersaturation results in droplet growth that rapidly dilutes the salt concentration in the droplets to 10^{-3} M or lower, AgI particles will survive as ice nucleants.

X-ray diffraction studies (Burkardt et al. 1970) have shown that melted mixtures of AgI and NaI form microcrystalline mixtures of AgI and NaI on cooling to ambient temperature. Mixtures of AgI and KI , however, form stable complexes on cooling from the molten state. Each particle of a composite $2\text{AgI} \cdot \text{NaI}$ aerosol becomes a microcrystalline mixture of its ingredients on cooling, with particle sizes substantially smaller than the original particle. When wetted, solution of these AgI microcrystals would be pronounced in high concentration NaI at water saturation. Their behavior under tran-

sient supersaturation conditions and rapid dilution of NaI solution droplets would allow nucleation to proceed before solution occurred. Wetting and decomposition of stable $2\text{AgI} \cdot \text{KI}$ complex particles would produce even smaller AgI particles after generation and cooling, thus explaining the very poor nucleating behavior of this composite nucleus aerosol.

b. *AgI and AgI · AgCl nucleus aerosols*

Increased ice nucleus activity of the $\text{AgI} \cdot \text{AgCl}$ nucleus compared to the AgI nucleus is conventionally attributed to improved structural match of the former with the ice structure (Vonnegut 1949; Palanisamy et al. 1986). The structural match relationship of ice and AgI , however, does not describe the molecular mechanism of nucleation. A structural match may be a requirement for nucleation in a manner not yet addressed experimentally.

We wish to develop an alternate hypothesis for the improved ice nucleus activity. Our hypothesis is based on the following analysis. First, silver chloride is almost 300 times more soluble ($8.9 \times 10^{-4} \text{ g L}^{-1} \text{ H}_2\text{O}$) than AgI ($3 \times 10^{-6} \text{ g L}^{-1} \text{ H}_2\text{O}$). If the more commonly used $\text{AgI} \cdot \text{AgCl}$ aerosol (0.78:0.22 ratio) contacts water droplets, then the AgCl will dissolve, at least in part. Second, the solution AgCl also will ionize completely (as does the AgI) but the large excess of Ag^+ ions over

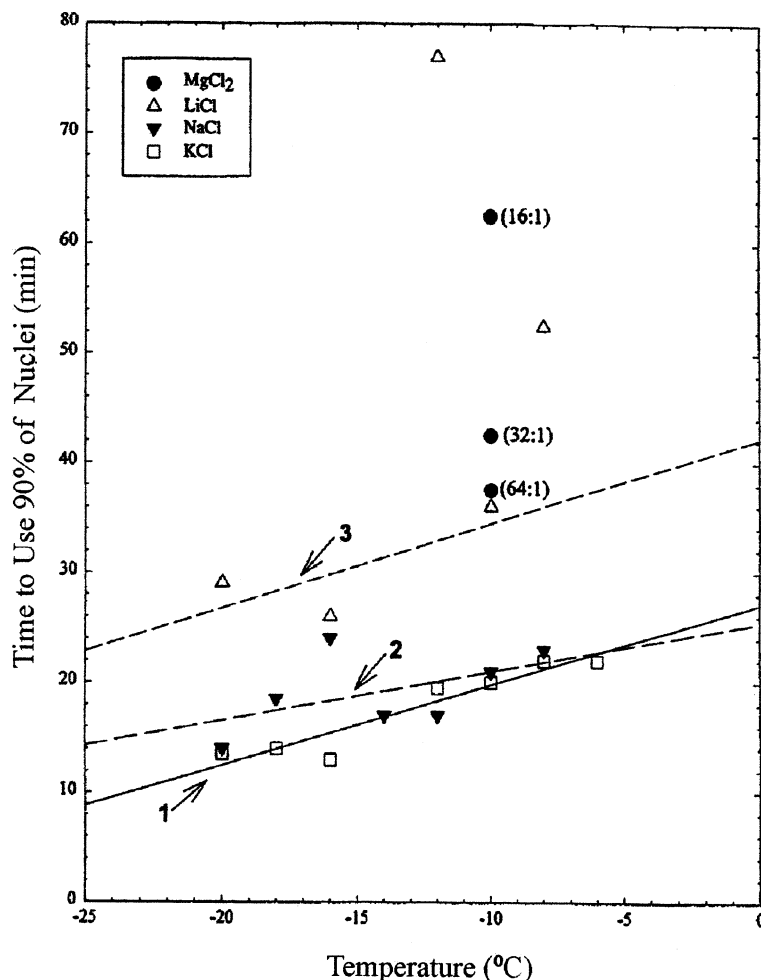


FIG. 6. Rates of depletion of ice nuclei concentration as a function of temperature for 1) $\text{AgI} \cdot \text{AgCl} \cdot 0.125 \text{ KCl}$ (plot 1), 2) $\text{AgI} \cdot \text{AgCl} \cdot 0.125 \text{ NaCl}$ (plot 2), and 3) $\text{AgI} \cdot \text{AgCl} \cdot 0.125 \text{ LiCl}$ nucleus aerosols. The rates at -10°C for various mole ratio $\text{AgI} \cdot \text{AgCl} \cdot \text{MgCl}_2$ aerosols are shown. The rates for $\text{AgI} \cdot \text{AgCl}$ aerosols functioning by the contact freezing mechanism are shown by the dashed line (plot 3). All nucleus aerosols were injected into the cloud chamber after diluted with -40°C dewpoint air. (From Finnegan 1998.)

I^- ions in solution ensures that the resultant AgI particle becomes less negatively charged than an AgI particle in the absence of AgCl . A lower negative charge on the AgI particle results in less dipole-dipole chain aggregation and greater hydrogen bonding of water molecules in the particle's hydration layer and hence, as hypothesized, faster nucleation. Third, faster nucleation permits smaller nuclei to function before they dissolve, thereby increasing the measured ice nucleus activity. Improved activity of the $\text{AgI} \cdot \text{AgCl}$ aerosol at temperatures of -10°C and warmer is indicative of the improved nucleation rate.

c. $\text{AgI} \cdot \text{AgCl} \cdot \text{alkali chloride composite aerosols}$

Silver iodide \cdot silver chloride \cdot sodium iodide ($\text{AgI} \cdot \text{AgCl} \cdot \text{NaCl}$) and KCl composite nucleus aerosols are

greatly superior to $2\text{AgI} \cdot \text{NaI}$ and $2\text{AgI} \cdot \text{KI}$ aerosols in both ice nucleus activities and rates of ice crystal formation at water saturation. Under transient supersaturation conditions, $\text{AgI} \cdot \text{AgCl} \cdot \text{NaCl}$ composite aerosols display increased ice nucleus activity, but the improvement is at temperatures of -10°C and above rather than -10°C and below. Rates of ice crystal formation are basically the same for two-nucleant systems, suggesting that the transient supersaturation technique dilutes salt concentrations to less than 10^{-3} M . The screening effect of the cations is nonexistent in either case. Under transient supersaturation conditions at -10°C , activity of the $\text{AgI} \cdot \text{AgCl} \cdot 4 \text{ NaCl}$ composite nuclei is fivefold greater than activity of the parent $\text{AgI} \cdot \text{AgCl}$ contact nuclei. This result suggests that in the contact nucleation process, smaller particles can dissolve in cloud droplets before they nucleate. In transient supersaturation in-

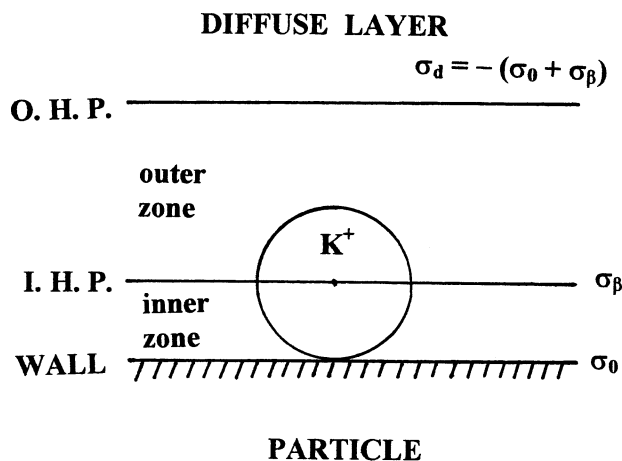


FIG. 7. Model of the electric double layer. OHP is the outer Helmholtz plane; IHP is the inner Helmholtz plane; σ_d is the total charge contained in a column of the diffuse layer of unit cross section; σ_β and σ_0 are the mean surface charge densities at IHP and the particle wall, respectively.

duced by the wet injection technique, smaller hygroscopic composite nuclei form smaller dilute solution droplets in which AgI particles will not dissolve and can therefore function.

The increased effect on activities and rates of ice crystal formation by alkali metal cations in the series $K^+ < Na^+ < Li^+$ is called a lyotropic effect. *Lyotropic sequence* is a term used to describe a sequence of ions, salts, or radicals arranged in descending order relative to the magnitude of their effect on a given solvent or system. In colloid chemistry, the term is normally used to describe differing colloid coagulation properties of alkali metal cations. In this work, the sequence is seen in the effect of varying alkali metal cations on ice nucleus activity and rates of ice crystal formation on composite AgI • AgCl • alkali chlorides. Specific properties of the AgI solution interface and cations leading to a lyotropic effect are not known.

The extreme effect of the alkaline earth Mg^{+2} cation on ice nucleation follows the Schulze–Hardy rule that divalent cations are an order of magnitude more effective than monovalent cations in a process such as colloid coagulation (Bijsterbosch and Lyklema 1978). Since rates of ice crystal formation and activity increase on exposure of these composite nuclei to transient supersaturations, slower rates at water saturation reflect different interferences of several cations on the nucleation step itself. Salt concentrations in the growing crystals are too low to interfere in the ice crystal growth process. The lyotropic effect is present only when the electric double layer is compact and vanishes when the layer becomes diffuse (Lyklema 1961). This appears to confirm the role of compact electric double layers and cationic screening on the nucleation step in ice crystal formation.

5. Summary of new hypothesis

Our analysis of the chemistry of AgI colloids and suspensions is the basis for a new hypothesis regarding the varied activities and rates of ice crystal formation of wetted AgI and AgI • AgCl aerosols, either alone or as composites with alkali halides. Our key point is that silver iodide colloid and suspension particles are electrically charged with Ag^+ and I^- as the potential determining ions. At dynamic equilibrium, these ions exist in solution around the particles and on particle surfaces as discrete patches. The net charge on pure AgI particles is negative from an excess of I^- ions. We hypothesize the nucleation mechanism of ice formation on AgI particles to be the random formation of embryos in patches of hydrated Ag^+ ions. Nucleation ability of the parent AgI particle is influenced by two factors: magnitude of the negative charge on the particle and presence or absence of a compact electric double layer on the particle surface. The presence of excess I^- ions (e.g., NaI or KI added in the composite nuclei) in the solution around the wetted particles increases particle negative charge. In turn, this increases the water dipole–dipole structure in a hydration layer on the particle surface, decreases the hydrogen-bonded structure of hydrated Ag^+ patches, and decreases ice nucleus activity as well as rates of ice crystal formation. Laboratory cloud chamber characterization studies have shown that the activity and rates of ice crystal formation of nucleus aerosols containing NaI or KI are decreased compared to composite nuclei containing NaCl or KCl, thereby supporting the hypothesis.

Conversely, the presence of excess Ag^+ ions in solution around the particles decreases the particle negative charge, increases the hydrogen-bonded structure associated with the Ag^+ hydrate patches, and decreases the dipole–dipole structure of the hydration layer. In colloid chemistry studies, addition of $AgNO_3$ was found to decrease particle negativity or charge it positively, depending on $AgNO_3$ concentration. In cloud chamber nucleation studies, AgI particle negativity was reduced by the addition of AgCl, which was cogenerated with AgI. Silver chloride is more soluble than AgI and adds Ag^+ ions without adding the other potential determining I^- ion. This composite AgI • AgCl nucleus is greatly superior to the AgI nucleus in ice nucleus activity at temperatures of $-10^\circ C$ and above. The nucleating component of the composite AgI • AgCl aerosol is AgI. The AgCl serves only as a source of Ag^+ ions in this interpretation of the nucleation mechanism on AgI. Again, these findings substantiate the validity of the hypothesis.

Concentrations of alkali iodides and alkali or alkaline earth chlorides of 10^{-2} M or greater in the solution phase of AgI colloids lead to formation of compact electric double layers at particle–solution interfaces. Alkali metal cations are attracted to this layer by the negative charge, and occupy positions in the Stern layer adjacent to the surface hydration layer. The alkali metal cations

screen movement of Ag^+ cations to and from the particles. Therefore, we further hypothesize that ice nucleus activity and rates of ice crystal formation at water saturation in cloud chamber tests decrease as a result of this screening and the resultant slowing of the nucleating step. Lithium cations have the greatest effect in the alkali metal series, and K^+ ions the least effect of the cations tested. This phenomenon, a lyotropic effect, results from specific but unknown properties of the different ions in the Stern layer.

When composite nuclei containing NaCl or KCl are exposed to transient supersaturations with respect to liquid water in cloud chamber experiments, rates of ice crystal formation and measured ice nucleus activity increase substantially at temperatures of -10°C and warmer, compared to results obtained at water saturation. These increases are attributed to dilution of alkali chloride concentration to 10^{-3} M or less in the solution around the particles. This is the concentration at which the electric double layer around the wetted particles becomes diffuse. A similar increase in the rate of ice crystal formation occurs for the same reason when composite nuclei containing NaI or KI are subjected to transient supersaturations. Ice nucleus activity is higher at -10°C and colder than is found in tests of this nucleus conducted at water saturation (compared to at -10°C and warmer for the alkali chloride composite nuclei).

Based on this analysis, a structural match between ice and AgI is not necessary for wetted AgI particles to function as ice nucleating substrates. The observation that an improved match coincides with improved activity may be entirely fortuitous.

The chemical kinetics approach to nucleation mechanism might be applied to the study of natural atmospheric nuclei. Little, if any, data are available on the rates of ice crystal formation using natural ice nuclei or their chemical compositions. Nevertheless, assuming that natural ice nuclei are clay minerals (i.e., silicates), the potential determining ions for wetted particles would be hydronium (H_3O^+) and hydroxyl ions (OH^-). If this is the case, then rates of ice crystal formation in naturally seeded clouds would be pH dependent, and clouds with high pH water (cloud droplets containing calcium carbonate, CaCO_3 , from included alkali dust) would behave differently than clouds containing acidic salts [e.g., ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$] in their now low-pH cloud droplets.

Acknowledgments. The authors wish to acknowledge the perceptive and constructive comments from the reviewers. The authors also wish to acknowledge the editorial assistance offered by Mr. Roger Kreidberg.

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