Heterogeneous Freezing Nucleation in Electric Fields

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ABSTRACT

Heterogeneous freezing nucleation in electric fields was studied on samples of water containing organic nuclei or silver iodide. Electric fields of 6000 V cm^{-1} (dc) were applied over sets of supercooled drops supported on a silicone varnish coated surface during different time-temperature sequences. In no case was a significant difference in the nucleation rates observed due to application of the field. It is concluded from these experiments that electric fields of up to 6000 V cm^{-1} have no intrinsic effect on the *heterogeneous* freezing process and that the probability of enhanced ice nucleation in the atmosphere due to natural electric fields is quite remote.

1. Introduction

The possibility that the nucleation of ice in supercooled water may be brought about by electric effects of various kinds has been amply demonstrated. Freezing due to the passage of electric discharges through the water was observed by Dufour (1861), Rau (1951), Schaefer (1953), Salt (1961) and Pruppacher (1963). Nucleation as a result of distortion or disruption of drops by electric forces was reported by Pruppacher (1963, 1973), Abbas and Latham (1969) and by Smith *et al.* (1971). When charged, aerosols and other surfaces coming in contact with drops were found to cause nucleation more readily than if no electric charge were present (Gabarashvili and Gliki, 1967; Roulleau *et al.*, 1971; Pruppacher, 1973). Electric fields also produced nucleation without macroscopically observable changes in the experiments of Rau (1951), Roulleau (1964) and Pruppacher (1973). In another class of experiments, electric fields and charges were demonstrated to be responsible for enhanced ice crystal production within supercooled fogs (Poc, 1967; Schaefer, 1968; Garraud, 1969; Roulleau *et al.*, 1971).

The inferences that were drawn from these experiments are just as varied as the experiments themselves. Dielectric polarization of water was postulated by Rau, Salt and by Gabarashvili and Gliki to be responsible for the observed effects. Nucleation in the thin liquid filaments which form during disruption of drops or during movement of drops on surfaces was suggested by Loeb (1963) and by Abbas and Latham as a possible mechanism. The observation by Abbas and Latham that mechanical disruption was as effective as disruption due to an electric field strongly favored this explanation. Cavitation was proposed by Smith *et al.* as the step that leads to ice nucleation. Motion of the triple-phase boundary, air-water-substrate, was found by Pruppacher (1963) to be essential for causing electro-freezing. In a recent study, Pruppacher (1973) discussed the theories described above, argued against them and put forward arguments which link electro-freezing to the formation of two-dimensional ice in disordered layers of adsorbed molecules. This latter concept was taken from Evans (1970).

The production of ice crystals by electric fields in cloud chambers was shown by Evans (1973) to be caused by fragmentation of dendritic crystals. Accelerated transport of charged water molecules to the crystal tips was given as the most plausible mechanism for enhancing growth in the electric fields.

It is important to find an adequate explanation for the influence of electric fields on ice nucleation and growth and to explore the varieties of situations where such effects occur, since these electric interactions can hold important clues to the fundamental processes of nucleation and growth. The large numbers of contradictory observations that have been reported and the tentativeness of all current explanations indicate the need for much further work. The present study was undertaken to provide contributions in two areas. First, it seemed worthwhile to augment previous tests, which used highly purified water with tests where the water would contain effective heteronuclei. Second, it was felt that the statistical significance of electro-nucleation should be assessed. The second aim required that tests be made using large numbers of samples and with reliably controlled experimental conditions. From the findings a better appreciation for the role of electro-nucleation was hoped to emerge. The tests with samples containing effective nuclei were planned to find out whether electric fields might influence the activities of

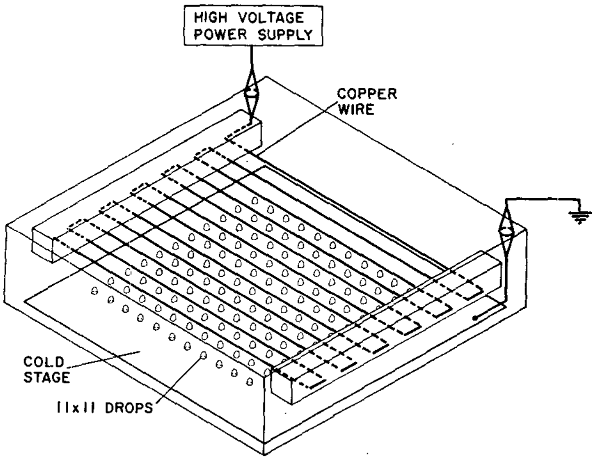

FIG. 1. Schematic of experimental arrangement. An array of 121 drops were placed on a grounded plate and a wire grid, 1 cm above the drops, served as the high voltage electrode. The outer plexiglass enclosure had dimensions of 12.5 cm×12.5 cm×4 cm.

such nuclei either through modification of the surfaces of the nucleants or through the alteration of the arrangement of water molecules. A major motivation for the experiment was to determine if the activities of natural ice nuclei in clouds, or of artificial seeding agents, might be affected by electric fields.

2. Experimental

The experimental set-up is shown in Fig. 1. Up to 121 droplets of 0.01 cm^3 volume were placed on a coated aluminum foil which covered a thermoelectrically cooled plate. The coating was a hard silicone varnish; comparison tests with various oils showed the nature of the coating to be of no consequence. An electric field was produced between the grounded plate bearing the drops and a wire grid located 1 cm above the drops. A dc field strength of 6000 V cm^{-1} was employed in all tests; it was felt that this was a reasonable upper limit for field strengths commonly occurring in atmospheric clouds. Routinely, the wire grid was at a positive potential with respect to the plate.

The salient features of the experimental arrangement were: 1) a nearly uniform field over the sample drops in a direction perpendicular to the supporting surface, 2) the use of an inert, solid, hydrophobic surface, and 3) the large number of drops observed simultaneously. While obviously not simulating atmospheric conditions entirely, the results ought to be valid for atmospheric situations. The use of a solid supporting surface was not considered to be a serious problem for examining the effects of the electric field on nuclei suspended in the drops. The experiments have, in fact, revealed no influence on nucleation by the electric field; there is no evident reason for questioning the applicability of these negative findings to atmospheric conditions.

Four different samples were tested: distilled water (DW), a suspension of leaf-derived nuclei (LDN), and two silver iodide colloids. The distilled water was singly-distilled with a freezing temperature range of -10 to $-26°C$ and a mean of $-20°C$ for drops of 0.01 cm^3 volume. The origin and nature of the DW nuclei is uncontrolled. The LDN nuclei were described by Schnell and Vali (1972); the sample used in the present experiments contained 10^{-4} g cm^{-3} of leaf matter. One of the silver iodide samples consisted of a precipitate of AgI from 1.73×10^{-6} g cm^{-3} of $3KI \cdot AgI$ complex, and the other contained 1.18×10^{-6} g cm^{-3} of commercial AgI powder. These samples were chosen to span a range of nucleating temperatures and electrical properties.

3. Results

Three different kinds of tests were made—the possibility of residual effects was examined, and the effects of fields during constant cooling and at constant temperatures were determined.

a. *Residual effects*

Tests were performed to determine whether an electric field applied for only a period prior to cooling of the drops could exert an effect. Residual effects thought possible were electrostatic precipitation of aerosols onto the sample drops or affectation of a permanent change at the surface of the nucleant.

For these tests, sets of drops were frozen, then melted and warmed to $+12°C$. The electric field was applied at that temperature for time intervals of 5 to 60 min. The field was then shut off, the droplets refrozen, and the freezing temperatures compared to those for the first cooling. Control experiments were made using an identical sequence but without applying the electric field.

First, the change ΔT in mean freezing temperatures was calculated for each pair of runs. No influence on ΔT as a function of the duration of the time lapse between runs could be detected. The average change $\overline{\Delta T}$ was obtained by combining all pairs of runs (six pairs per sample) and the standard deviation (SD) of the ΔT values about $\overline{\Delta T}$ calculated. The first two columns in Table 1 list for each sample these $\overline{\Delta T}$ and SD values. The freezing temperatures of the first run of each pair were compared with those of the second run for each drop to ensure that the mean temperature changes do not conceal some significant changes in opposing directions. The coefficient of correlation (R) between all temperature-pairs was calculated; the approximate equality of these coefficients for the experiments with and without electric fields shows that no significant change was brought about by the field. The same conclusion is reached by calculating the significance of the observed difference between the $\overline{\Delta T}$ values for runs in which the field was applied and the $\overline{\Delta T}$

Table 1. Changes in freezing temperatures (°C) and correlation coefficients R between successive refreezings of drops for pairs of runs with and without application of an electric field between runs.* See text for identification of terms.

	DW			LDN			3KI·AgI			AgI		
	$\overline{\Delta T}$	SD	R	$\overline{\Delta T}$	SD	R	$\overline{\Delta T}$	SD	R	$\overline{\Delta T}$	SD	R
With field	−0.59	0.79	0.75	+0.03	0.30	0.88	+0.06	1.01	0.42	+0.09	0.99	0.35
Without field	−0.74	0.98	0.72	−0.15	0.17	0.81	−0.46	1.01	0.25	−0.96	1.84	0.35
Significance of field effect		22%			75%			62%			74%	

* $\overline{\Delta T}$ is negative if mean temperature for second run is warmer than for first.

values for the controls (22, 75, 62 and 74% for the four samples).

b. *Field applied during cooling*

Sequences of tests were made in which the electric field was alternatively applied or left off during the cooling of the drops. Cooling was at a constant rate of 4°C min^{-1} for all runs. Results for these tests are given in Figs. 2 and 3.

Fig. 2 shows the mean freezing temperatures of runs in four different sequences. Though definite trends are observed for AgI and for 3KI·AgI nuclei, these trends are seen to be independent of the electric field and have been found by Vali and Finnegan (1970) to be frequently present in refreezing experiments of this type. No significant changes are evident for LDN and DW nuclei. The differences between the overall mean temperatures of all runs with and without the electric fields were 0.11, 0.32, 0.05 and 0.01°C, for AgI, 3KI, LDN and DW, respectively; the statistical significances of these differences are only 25, 30, 20 and <5%. It is thus seen that the mean freezing temperatures of the nucleants were not discernably influenced by the electric field.

Fig. 3 shows histograms of the changes in freezing temperatures between successive runs (with and without the field) for individual drops. In this presentation an effect of the electric field would be manifested by skewness in the histograms. The symmetry of the histograms indicates that run-to-run changes were random and that the conclusion drawn for the average temperatures applies to each of the individual specimens also.

c. *Tests at constant temperatures*

It was thought that the sensitivity of the tests could be increased by making observations of the rate of nucleation at fixed temperatures, as opposed to the continuously cooled experiments described in the previous section. This was the type of test used in most

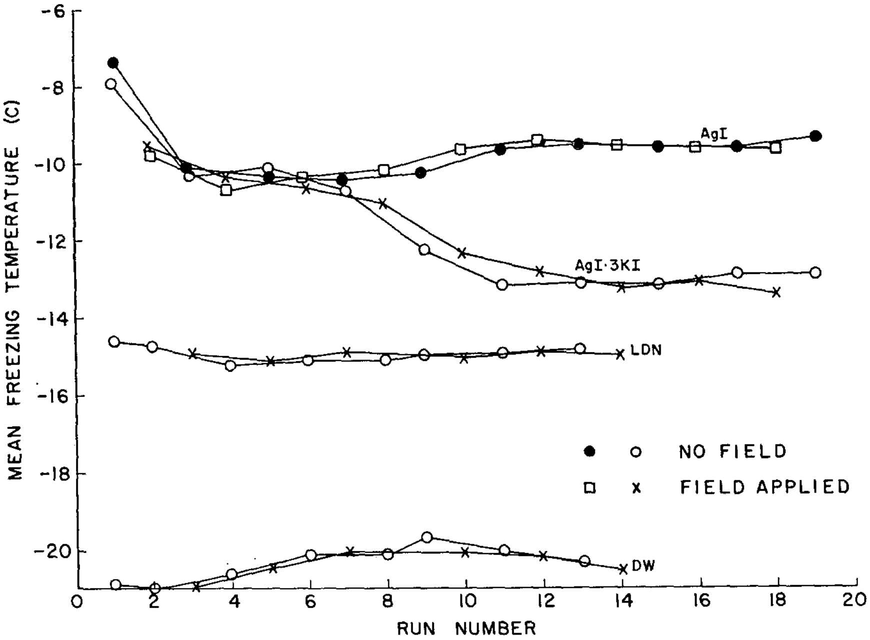

Fig. 2. Mean freezing temperatures for four samples in sequences of refreezing in which the electric field was applied in every other run. Lines on the graph connect the no-field and field-on points; the near overlap of the two lines for each sample demonstrates the absence of noticeable effect by the field.

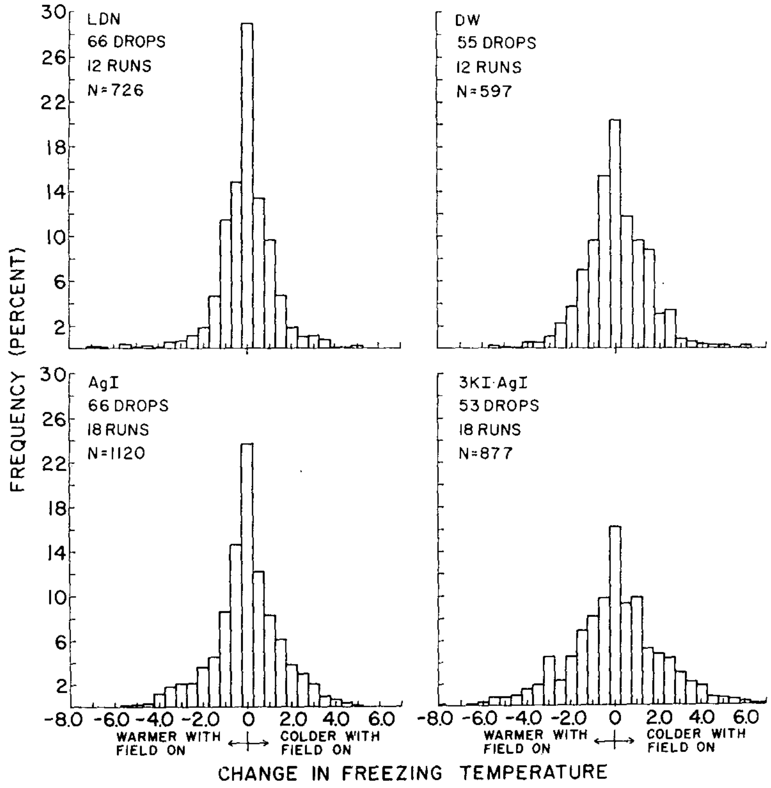

FIG. 3. Histograms of the changes in freezing temperatures between successive runs (with and without the field) for individual drops for the same samples as in Fig. 2.

previous researches. A drawback of this procedure is that the number of drops freezing in a given test is small so that it is difficult to establish statistical significance.

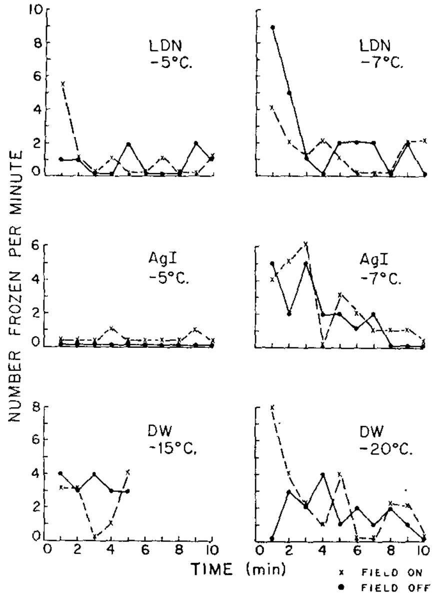

FIG. 4. Average rate of nucleation in two runs at fixed temperature with and without an electric field of 6000 V cm^{-1}. Points represent rate for preceding 1-min interval.

Fig. 4 presents the results of tests in which the sample drops were cooled to some temperature and the field was then applied. The rate of freezing of drops was recorded and compared to control tests in which the electric field was absent. In each experiment there were at least 110 drops not yet frozen at the beginning of the period of observation. The points plotted are for the averages of two runs. Scrutiny of the data in Fig. 4, as well as statistical analysis, show no systematic influence attributable to the electric field.

From previous reports it appeared that nucleation might be initiated more readily at the moment of application of an electric field than with a steady field. To test this possibility, i.e., the effects of transient fields, experiments were performed in which the field was turned on and off at 2-min intervals. Fig. 5 shows the rate of freezing of drops (at −5°C) under such conditions. The lack of any repetitive pattern again indicates the absence of an effect of the electric field on the nucleation process.

4. Discussion

The results of the present experiment, when contrasted with earlier findings, pose a dilemma: why were there no observable effects ascribable to the electric fields in our experiment, whereas there is such extensive evidence in the literature for the existence of electric influences on freezing nucleation? First, it should be

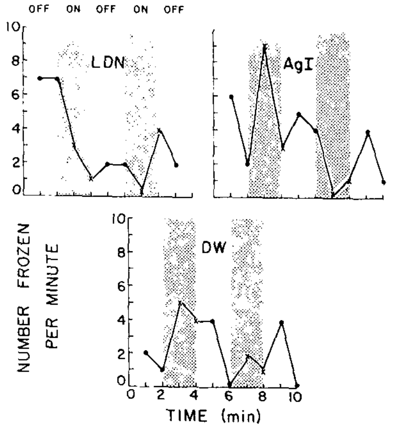

FIG. 5. Rate of nucleation during intermittent application of 6000 V cm^{-1} of electric field at $-5°C$ for LDN and AgI and $-10°C$ for distilled water (DW). Points represent rate for preceding 1-min interval.

pointed out that several earlier reports have emphasized the unpredictability of electro-freezing. Only with radical interferences, like the passing of a discharge directly through the water, was freezing invariably observed. (This effect was also evidenced in our tests: when an arc-over occurred to a drop, that drop froze.) Our experimental arrangement excluded the possibility of freezing due to disruption, cavitation or gross motion of interfaces.

Our experiments were most similar to those of Roulleau (1964). In both cases the drops were exposed to uniform electric fields of comparable magnitudes, while supported on flat solid surfaces. In Roulleau's experiments, the drops were surrounded by oil, in ours by air. She noted perceptible deformation of the drops by the electric field, we did not; this difference might account for the contradictory findings. This explanation would follow from the suggestion of Pruppacher (1963) that motion at the water-substrate interface was a necessary condition for electro-freezing. In Pruppacher's experiments, the electric field always produced deformations of the water samples. Another possible origin of the discrepant findings might lie in the nature of the substrates used: Roulleau used oil over glass, Pruppacher used mostly polyethylene, and we used a solid silicon varnish (in some exploratory tests with polyethylene sheets we found difficulties with ice spreading rapidly along the surface). Whatever the reason may be for the differences between experiments, there is no reason to suggest that an influence which could affect drops in the atmosphere was somehow masked in the present tests.

From our experiments we conclude that electric fields of up to 6000 V cm^{-1} have no *intrinsic* effect on the *heterogeneous* freezing process (at least for LDN and AgI nuclei). Continued efforts must clearly be made to explain the origins of the effects of electric fields in those experiments where they were observed. In accordance with other authors, we conclude that the probability of ice formation in atmospheric clouds due to natural electric fields is quite remote. We have extended the validity of this conclusion to include situations involving the presence of active heteronuclei.[1]

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[1] *Note added in proof*: A recent paper by G. A. Dawson and G. R. Cardell (Electro-freezing of supercooled waterdrops, *J. Geophys. Res.*, **78**, 8864–8866, 1973) describes experiments with water drops suspended in an airstream and subjected to electric fields. Their conclusions are essentially the same as those described in this paper.