Freezing nucleation in aqueous electrolytes

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ABSTRACT

Experiments were performed to determine the extent to which the nucleating abilities of artificial and natural freezing nuclei are influenced by the presence of salts dissolved in water. Four different nucleants (at fixed concentrations) were tested in combinations with 10–20 soluble salts using the drop freezing technique. Changes in freezing temperatures were determined for each nucleant–salt combination at salt concentrations of 0, 0.01, 0.1 and 1 molal. Major differences were noted in the responses of the different nucleants and it was concluded that the influence of dissolved salts on heterogeneous freezing nucleation is not due to changes in the bulk water structure, but results from modifications at the nucleant–embryo interface. The measurements indicate that the salt contents of cloud droplets can be expected to alter the ice nucleating activities of suspended particles by as much as ± 4°C.

I. Introduction

Since natural cloud condensation nuclei (CCN) are generally composed of soluble salts, and since cloud droplets collect additional soluble aerosols throughout their lifetimes, salt content is an inescapable factor which will have bearing upon the heterogeneous freezing nucleation of cloud droplets in the atmosphere. Furthermore, in attempting to induce modification of precipitation processes with artificial ice nuclei, if the generator effluent contains appreciable amounts of soluble materials the ice nucleating properties of the seeding material may be affected.

It has already been demonstrated in the laboratory that dissolved salts present in water may influence the effectiveness (the temperature of nucleation) of freezing nuclei.[1] In a few studies nucleants were deliberately introduced into the samples (Hoffer, 1961; Edwards & Evans, 1962; Evans, 1967; Wood & Blair, 1968; Vali & Finnegan, 1970; Ramachandra Murty & Ramana Murty, 1972) but in the majority of experiments the water was purified to eliminate particulates (see references in Table 1). Actually, for most of the latter cases, the distinction is only one of degree, since in fact the water samples must have contained some particles, as evidenced by the fact that the freezing temperatures observed were considerably above the temperature of homogeneous nucleation. Table 1 presents an overview of the results of experiments which used purified water. In three of the experiments homogeneous nucleation was being observed (frezing temperatures below -35°C), in the others, the mode of nucleation was heterogeneous. The large scatter in the freezing temperatures of the water samples is indicative of differences in particulate contents and at least partially explains the divergent effects reported for the salt solutions. There is agreement with respect to NH_4I and NaI; additions of these salts in all cases led to freezing temperatures more than 1°C warmer than those of the pure water used.

More relevant to natural or induced glaciation processes in clouds are probably the studies with specific nucleants. Hoffer (1961) examined the effect of a mixed solution of $MgCl_2$ and Na_2SO_4 (to simulate natural CCN) on the nucleation temperatures of AgI, illite, montmorrillonite, halloysite and kaolinite. He found that nucleation temperatures were depressed, the depression being greatest for saturated

[1] Immersed particles which are capable of initiating the liquid-to-solid phase transition of water.

Table 1. *Summary of materials found active or inactive in promoting nucleation of "purified" water*

Investigator(s)	Method	T_m (°C)[a]	Drop Size (Diameter)	$T > Tm + 1$[a]	$T \leq Tm + 1$[a]
Heverly (1949)	Cloud[b] chamber	−29	0.1 mm	None reported	NaCl
Lafargue (1950)	Drop freezing	−40.5	1 to 10 μ	None reported	NaCl KI, $MgCl_2$ $ZnCl_2$
Hosler (1951)	Cloud chamber	−24	$\leq 50\,\mu$	NaI, NH_4I, $AgNO_3$	NaCl, $Pb(NO_3)_2$
Bigg (1953)	Drop freezing	−24	0.1 to 5 mm	HF, LiF, NaF, KF, HCl, LiCl, KCl, CsCl, HBr, NaBr, KBr, HI, LiI, NaI KI, NH_4I, $LiNO_3$, $NaNO_3$, KNO_3, $CsNO_3$, NH_4NO_3, Li_2SO_4, Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$	CsF, NaCl, LiBr, CsBr, CsI, H_2SO_4
Hosler & Hosler (1955)	Capillary tube	−20.1	0.25 to 3 mm	KI, NH_4I, $AgNO_3$, $CaCl_2$	NaCl
Kiryukhin & Pevsner (1956) As reported by Hoffer (1961)	Data not available			None reported	NaCl
Lafargue (1958)	Capillary tube	−19	1 mm	LiCl, NaCl, KCl, RbCl, CsCl, NH_4Cl, $MgCl_2$	None reported
Sano et al., 1960	Cloud chamber	−27	3 to 15 μ mean = 8 μ	NaCl, KCl, $BaCl_2$, $AlCl_3$, NaBr, KBr, $BaBr_2$, $AlBr_3$, NaI, KI, BaI_2	None reported
Hoffer (1961)	Cloud chamber	−36	50 to 200 μ	None reported	Na_2SO_4, K_2SO_4, $MgSO_4$, and "Mixed" $Na_2SO_4 + MgCl_2$
DePena et al., 1962	Drop freezing	−22.5	0.5 to 2.6 mm	KF, NH_4F, HI, NaI KI, NH_4I	LiF, NaF, HCl, LiCl, NaCl, KCl, NH_4Cl, HBr, LiBr, NaBr, KBr, NH_4Br, LiI, NH_4OH
Pruppacher & Neiburger (1963)	Drop freezing	−24	2 mm	NH_4I	HF, KF, CsF, NH_4F, LiCl, NaCl, KCl, CsCl, NH_4Cl, LiBr, KBr, CsBr, NH_4Br, HI, LiI, KI
Uzu & Sano (1965)	Cloud chamber	−28	5 to 15 μ	CsF, KCl, CsCl, NaBr, KBr, CsBr, LiI, NaI, KI, RbI, CsI, Na_2SO_4, K_2SO_4, $CuSO_4$, K_3PO_4	NaCl, $BaCl_2$, $BaBr_2$ $(NH_4)_2SO_4$, $MgSO_4$
Wood & Walton (1969)	Drop freezing	−36.7	2 to 50 μ	None reported	KF, HCl, LiCl, NaCl, KCl, RbCl, CsCl, KBr, KI, CsI

[a] T_m is the mean freezing temperature for the "purified" water used.
[b] Droplets sprayed into a cold-box.

solutions and barely noticeable for solutions at 1/1,000 of saturation.

Edwards & Evans (1962) studied the effects of varying concentrations of Ag^+ and I^- ions on AgI hydrosols. They found that nucleation occurred with the least supercooling in solutions of 10^{-5} m $AgNO_3$ whereas in the presence of dilute KI increased supercooling was required for nucleation. Based on these results, it was suggested that the most favorable situation for nucleation is to have a minimum of surface charge (isoelectric point) which for AgI occurs at 10^{-6} molar $AgNO_3$. Evans (1967) reported that the nucleation temperatures of phloroglucinol dihydrate were progressively raised in 1 to 2-molar NaCl solutions. To explain these results, the existence of a monolayer of ordered water molecules on the surface of the nucleant was postulated; the effect of increasing salt concentration was assumed to encourage 2-dimensional crystallization of the monolayer. Vali & Finnegan (1970) measured the nucleation temperatures of 0.4 mole of AgI in a 4 molar solution of KI and of varying dilutions of this solution. The nucleation temperatures of the successive dilutions were found to rise until a leveling off at about 0.07 mole AgI and 0.7 mole KI. Reduction in melting point depressions and continued precipitation of AgI were believed to be responsible for these results.

Ramachandra Murty & Ramana Murty (1973) found that soluble salts exhibit a wide range of influence upon the nucleation behavior of AgI. They attempted a qualitative explanation of these findings based on a reduction of surface free energy at a nucleant surface due to the presence of polarized solute ions.

The studies cited above constitute fairly clear evidence that dissolved materials can appreciably influence heterogeneous freezing nucleation although the reasons for this are not well understood. Since the effects were found to be specific to each nucleant tested, and were also different from those reported for purified water, one may tentatively draw the conclusion that the changes in nucleating ability were due to interactions of nuclei with the dissolved ionic species.

Although all of the tests discussed here used some form of dropfreezing technique there were sufficient differences in methods to make comparisons difficult. Also, due to the tediousness of drop-freezing experiments, the sample sizes

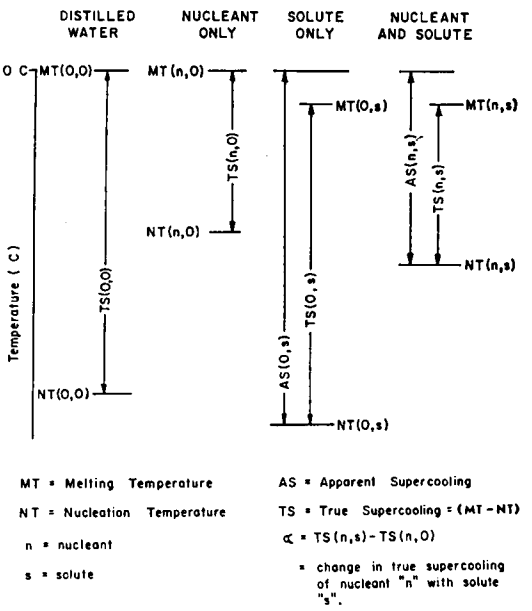

Fig. 1. Definitions of the quantities involved in the nucleation experiments with nucleant–salt combinations.

dealt with were small in most experiments. Pruppacher (1963) called attention to the need to eliminate nucleating particles that may be introduced with the soluble salts; this was not done in some of the other experiments. As a result, there is considerable uncertainty attached to many of the reported results. Because of improvements in the technique of drop freezing experiments and in their quantitative evaluation beyond relative comparisons (Vali, 1971) and because the need was felt for a more comprehensive study of the effects of dissolved salts on different nucleating substances the present study was undertaken. More specifically, it was felt necessary to evaluate solute effects on specific nucleating substances, so that the ambiguity, whether the observed effects are due to modifications of the structure of water, changes of activity of nucleating particles or the inadvertent addition of nuclei with the soluble salts, could be removed.

1. Theoretical framework

Materials which are effective as ice nucleants are generally only slightly soluble in water (although exceptions such as phloroglucinol

are known) and thus do not alter the melting temperature to nearly the same extent as they influence the nucleation temperatures. Solutes affect the melting temperature but will not by themselves serve as nuclei, although the homogeneous nucleation threshold is changed due to modification of the structure of the liquid (Wood & Walton, 1969). Adding solutes to a suspension of nucleating particles may influence both melting and nucleation temperatures: the melting temperature is invariably lowered while the effects on nucleation are less predictable. An assessment of the effects of soluble salts on heterogeneous nucleation must be made in terms of both the nucleation temperatures and melting temperatures.

Discussion will be facilitated by the introduction of a number of definitions, as shown in Fig. 1. Melting temperatures (MT) and nucleation temperatures (NT) are the two basic measured quantities. Apparent supercooling (AS) is defined as the magnitude of the supercooling required for nucleation below 0°C. The true supercooling (TS) is the magnitude of the difference between the melting and nucleation temperatures. It is believed that true supercooling is the best measure of the nucleating capacity of a material. The work of Evans (1965), as well as the results of this study support the assumption implied in the use of TS, i.e., that AS = TS + MT is meaningful and that TS is independent of MT. The change in true supercooling for nucleant n, due to solute s, is denoted by $\alpha(n, s)$ and is the difference in TS between a sample containing nucleant only $(n, 0)$ and the TS for the sample with the solute added. A value of $\alpha < 0$ implies that the salt reduced the amount of supercooling necessary to initiate nucleation (since TS is defined as a positive quantity).

It may be noted that $\mathrm{MT}(n, s)$ is not necessarily equal to $\mathrm{MT}(0, s)$ due to the possibility of adsorption of ions onto the nucleant surfaces, and/or partial dissolution of the nucleant. Consequently, it is of importance to determine $\mathrm{MT}(n, s)$ directly for each sample, especially if the nucleant is in high concentration.

2. Experimental design and procedures

(a) *Materials*

It seemed desirable to test a selection of nucleants, some of natural occurrence and also some of relevance to cloud seeding. The materials chosen for these experiments were: kaolin (KLN), leaf-derived nuclei (LDN), silver iodide (AgI) and cupric sulfide (CuS). The CuS nucleant was Analytical Reagent Grade and was ground with mortar and pestle before preparation of a stock suspension. To produce the AgI suspension, 3KI·AgI (obtained from the Naval Weapons Center, China Lake, California) was dissolved and AgI precipitated by dilution. The LDN were derived from decayed spruce (*Picea gluaca*) leaves by aqueous extraction. The KLN was a washed and ignited powder of technical grade kaolin which was ground with mortar and pestle before preparation of the stock suspension.

Stock suspensions of the four neucleants were prepared at the following concentrations:

KLN: 2.0 g/liter
LDN: 5.0×10^{-1} g/liter
AgI: 6.2×10^{-3} g/liter
CuS: 4.0 g/liter

For use as soluble salts, the alkali halides were chosen since these include a number of components of sea salt (which is a major contributor to natural cloud condensation nuclei), offered a convenient variation of ion size, and also include the solubilizers of AgI in common use for cloud seeding solutions. A number of ammonium salts were also tested because of their relative abundance in natural aerosols. Tests were also made with a few sulfates and nitrates and a sample of sea salt. Reagent Grade purity salts were used as received from the manufacturer. The sea salt sample was obtained by evaporating a quantity of ocean water (the molecular weight was taken to be that of NaCl).

The water used in the tests was taken from a glass laboratory still. Nucleation temperatures (T_{90}, see following sections) varied between −23 and −26°C. These temperatures are considerably lower (by 5 to 10°C) than those of the hydrosols tested so that further purification was not necessary in order to avoid interference with the nucleation measurements. Foreign materials, both particulates and dissolved matter, were undoubtedly present in the water, the possible influences of these on the solute nucleant interactions is undetermined. In this respect the water used was somewhat similar

to cloud droplets in equilibrium with the natural atmosphere.

(b) Sample preparation

Salt solutions (0.02, 0.2 and 2.0 molal) were first prepared by weighing and mixing the appropriate amounts of salt and distilled water. Immediately before testing, a portion (1 to 2 g) of the selected nucleant stock suspension was weighed and an equal weight of salt solution added. Thus, the final salt concentrations became 0.01, 0.1 and 1.0 m; final nucleant concentrations were one-half of the values given above. These nucleant concentrations apply to all tests.

(c) Measurements. Melting temperatures were determined using a method similar to that used for cryoscopic determination of molecular weight (Shoemaker & Garland, 1967). The temperature of a well-stirred test solution was monitored with a copper-constantan thermocouple while the sample was gradually cooled. The output of the thermocouple was recorded on a chart recorder and the melting points were deduced by an extrapolation of the liquid–solid equilibrium temperature during solidification to the initial cooling-curve of the brine.

Nucleation temperatures were determined using the nucleus spectrometer (Vali & Knowlton, 1970). This instrument consists of a thermally controlled cold-plate and appropriate peripheral instrumentation for monitoring and recording the freezing of drops placed on the plate, detected through the change in transparency of the drops. For each test, 121 equal-sized drops (0.012 cm^3 $\pm 5\%$) were placed on the cold stage over an aluminum foil coated with dry silicone resin. A constant cooling rate of 3.6°C min^{-1} was maintained during the experiments.

Measurements of individual freezing temperatures on the nucleus spectrometer were accurate to within ± 0.05°C. Temperatures for a given run of 121 drops were reliable within about ± 0.2°C because of statistical sampling factors. When the results of several runs are combined the accuracies are dominated primarily by sample variabilities. Normally the results of two consecutive runs were combined if the temperature at which 90% of sample drops were frozen (T_{90}) agreed to within 1°C; if not, a third test was made and the two runs showing the closest agreement were used. The two T_{90}-temperatures finally used typically agreed to within 1°C; the difference was in no case more than 2°C. These differences were attributed to sedimentation losses or aging and introduced an average uncertainty of about ± 0.5°C in T_{90}.

Table 2. *Melting point depressions (C) for nucleant–salt combinations*

	0.1 m		1.0 m	
Salt	DW*	N	DW*	N
NaCl	0.4	0.4	3.4	3.4
KF	0.4	0.3	2.7	2.6
KCl	0.3	0.4	3.4	3.2
KBr	0.4	0.3	3.0	2.4
NH_4F	0.3	0.3	2.0	2.1
NH_4Cl	0.3	0.3	2.7	2.7
NH_4Br	0.2	—	2.1	—
NH_4I	0.3	0.4	3.0	3.0
NH_4CNS	0.2	—	2.0	—
$(NH_4)_2SO_4$	0.5	0.5	3.4	3.5

[a] No nucleants intentionally added.
[b] Averages for LDN and AgI combined.

The accuracies of the measured melting points, as determined by repeated measurements (up to 5), are about ± 0.1°C for the 0.1 m samples and about ± 0.2°C for the 1.0 m samples. These variations are less than the other variabilities in the experiments.

(d) Derived quantities from the drop-freezing experiments

Concentration versus temperature functions, or nucleus spectra were derived as given by Vali (1971).

The differential spectra, $k(\theta)$, describe the concentrations of nuclei active in a unit volume of sample within a unit temperature interval about temperature θ:

$$k(\theta) = \frac{1}{VN(\theta)} \frac{dN}{d\theta} \ [\mathrm{cm^{-3}C^{-1}}] \qquad (1)$$

where

V is the drop volume,
$N(\theta)$ is the number of drops still unfrozen at the temperature θ.
dN is the number of drops freezing during the temperature interval $d\theta$.

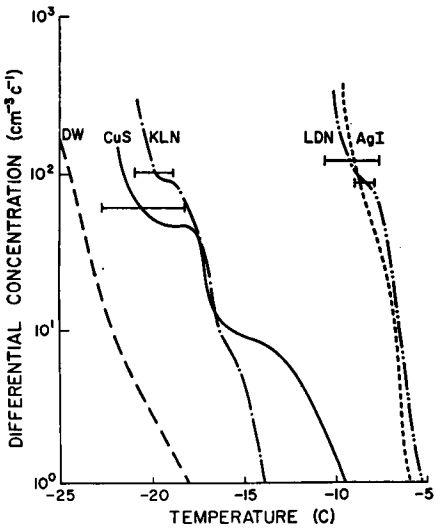

Fig. 2. Differential nucleus spectra for the four nucleants. Bars on spectra indicate range of T_{90} for for each nucleant.

By integrating eq. (1) from 0°C to θ, cumulative spectra which give the concentration of nuclei active at all temperatures warmer than θ can be obtained:

$$K(\theta) = [\ln N_0 - \ln N(\theta)]/V \ [\mathrm{cm}^{-3}] \qquad (2)$$

where $N(\theta)$ and V are the same as in equation (1) and N_0 is the total number of drops in the experiment.

For ease of comparison of large numbers of different samples, it is convenient to use a single measure of nucleus content rather than the entire spectrum. The temperature at which 90 % of the sample drops in a given experiment are frozen, T_{90}, provides one such measure. This quantity can be readily determined during the progress of an experiment and has relatively good statistical significance. It can be shown, using (2), that T_{90} corresponds to a particular value of $K(\theta)$: for $N(\theta) = 0.9N_0$ and $V = 1.2 \times 10^{-2}$ cm³, T_{90} correspond to the temperature above which there are 192 active nuclei per cm³.

3. Results

(a) *Melting points*

The results of the melting-point determinations are presented in Table 2. Each value in the table is the average of from two to eight independent measurements. Slight reductions in melting point depression were evident for solutes mixed with nucleants. The changes were essentially the same for the different nucleants.

In some cases, even for pure solutions, the measured melting point depressions were less than values reported in the literature by up to 0.2°C for the 0.1 m solutions and by up to 1.0°C for the 1.0 m solutions. Thus, both because of differences from tabulated values and because of the effects of nucleants on the melting points, use of measured melting points has clear advantages. Even so, for the sake of expediency, some of the melting points used in this work were taken from the literature. The resultant uncertainties in melting points are comparable or smaller than the variabilities of freezing temperatures of the nucleants.

(b) *Nucleation measurements*

Nucleants in pure water. Differential nucleus spectra for the four nucleant samples are shown in Fig. 2. These spectra represent the median of the results of a number of tests and the bars indicate the range of T_{90}-temperatures for all runs with a given nucleant.

As Fig. 2 reveals, the four nucleants fall into two groups with respect to activity: LDN and AgI are rather active nucleants, while KLN and CuS may be regarded as inactive.

Pure solutions. Pruppacher & Neiburger (1963) found that some nucleating particles are often found even in Analytic Reagent Grade soluble salts. Therefore, all solutions were tested prior to their use in mixtures with nucleants. Nucleus concentrations were found sufficiently low to be of no consequence in contributing to the nucleus contents of the salt-nucleant mixtures. For the RbCl and the sea-salt solutions it was necessary to remove unwanted particles by filtration.

Since the salt solutions in distilled water resembled the kind of samples that were used in many previous experiments, the measured nucleation temperatures of the salt solutions at different salt concentrations have some intrinsic interest also. Fig. 3 shows true supercooling (T_{90}-values) as function of salt concentration for the 23 salt solutions tested. The data are grouped by anion with the exception of the ammonium salts. In general, changes in T_{90} due to the added salts are small, although some large changes are indicated.

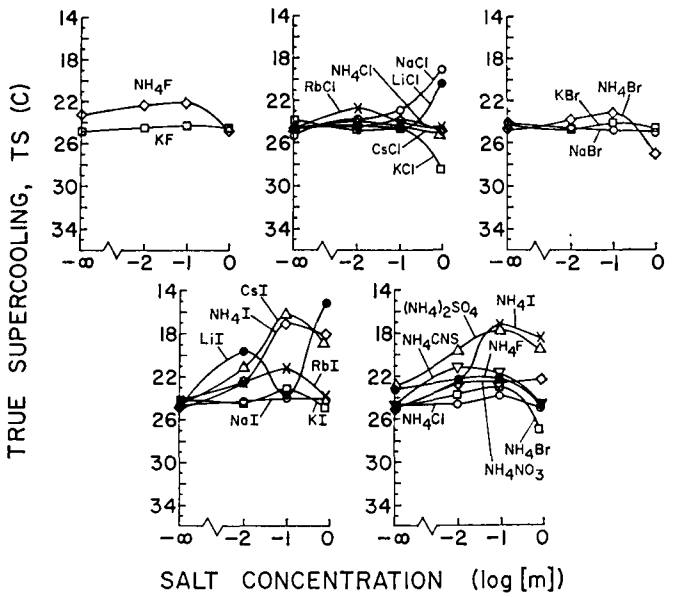

Fig. 3. True supercooling as a function of salt concentration for fluoride, chloride, bromide, iodide, and ammonium salt solutions. Note that TS increases downward corresponding to colder freezing temperatures.

The iodides exhibited the smallest true supercoolings. LiI, CsI and NH_4I showed exceptionally small true supercoolings. A minimum in supercooling is evident at 0.1 m salt concentration for the iodides with large cations (i.e., Rb^+, NH_4^+ and Cs^+); the ammonium salts also show a minimum at 0.1 m with the exception of NH_4NO_3 and NH_4CNS.

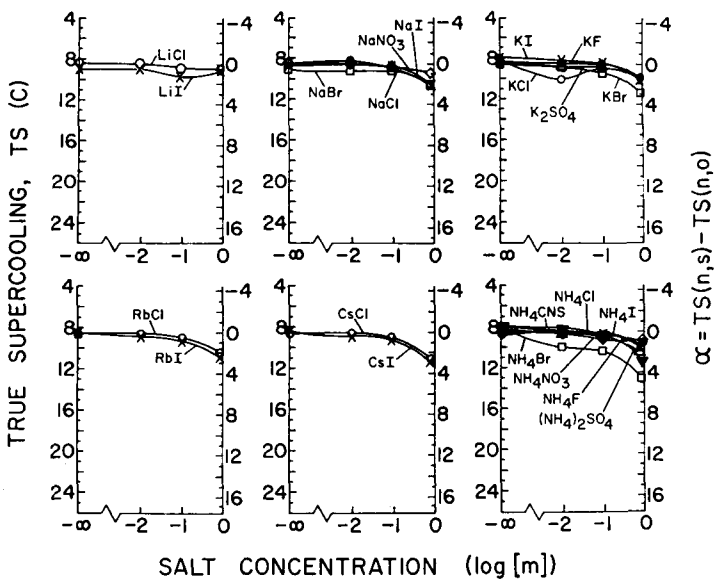

Fig. 4. True supercooling as a function of salt concentration for LDN hydrosols with lithium, sodium, potassium, rubidium, cesium, and ammonium salts.

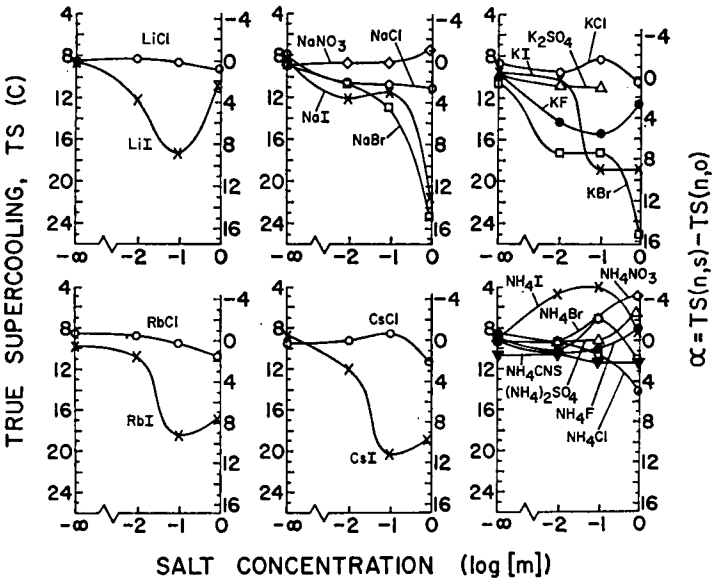

Fig. 5. True supercooling as a function of salt concentration for AgI hydrosols with lithium, sodium, potassium, rubidium, cesium, and ammonium salts.

One weak trend appears to be present: the ammonium cation is generally associated with the smallest true supercooling for a given anion. There is also a hint that the iodide anion has smaller true supercoolings for given cations than other halides. These results are in accord with the majority of the data reported in Table 1.

Nucleant–salt combinations. The different

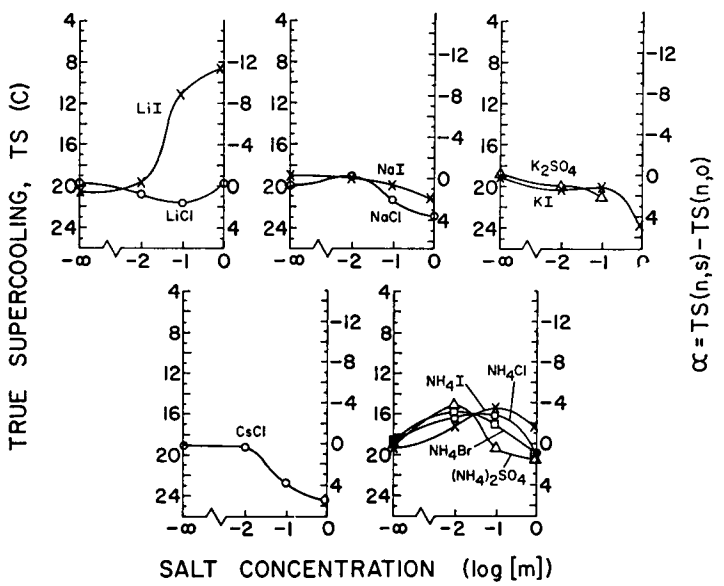

Fig. 6. True supercooling as a function of salt concentration for KLN hydrosols with lithium, sodium potassium, cesium, and ammonium salts.

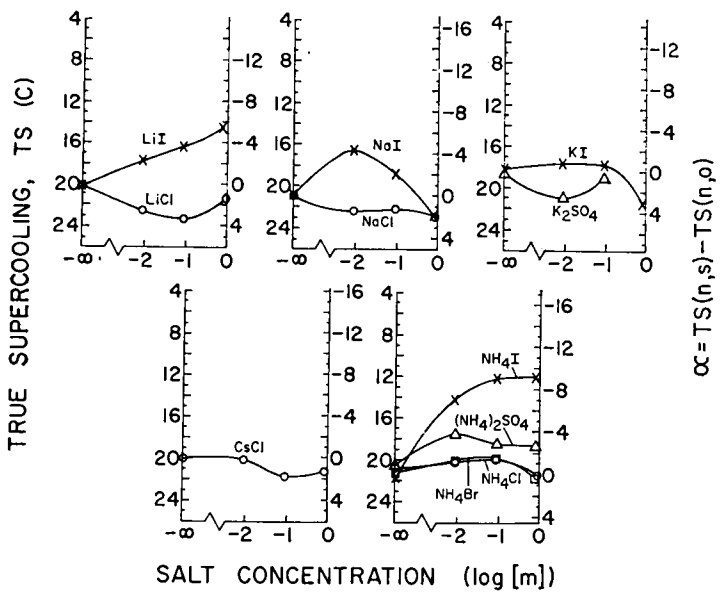

Fig. 7. True supercooling as a function of salt concentration for CuS hydrosols with lithium, sodium, potassium, cesium, and ammonium salts.

nucleant–salt combinations which were tested are listed in Table 3. The results of the measurements are given in Figs. 4 through 7. For each nucleant–salt combination, true supercooling (shown on the left-hand ordinate) and α (shown on the righthand ordinate) are plotted as functions of salt concentration. The $\alpha = 0$ points in these diagrams correspond to the average of T_{90}-temperatures for nucleant suspensions without salt taken from tests concurrent with the tests for the salt solutions in a given graph.

In general, the presence of salts increased the true supercooling, but exceptions are not rare and are of special interest. The different nucleants respond in characteristic ways so that presentation of the results is grouped according to nucleants.

In comparison to the three other nucleants studies, LDN exhibited a unique pattern of response. With few exceptions, LDN show very small changes in true supercooling, generally less than 1.5°C, with a tendency toward greater supercoolings with 1 m salt concentrations. This uniformity of behavior exhibited with such a large number of different salt types is quite remarkable. Even the largest changes observed, for the bromide salts, are quite small compared to the variations observed for the other nucleants.

Table 3. *Nucleant–salt combinations tested*[a]

	F^-	Cl^-	Br^-	I^-	NO_3^-	CNS^-	$SO_4^=$
Li^+		LAKC		LAKC			
Na^+		LAKC	LA	LAKC	LA		
K^+	LA	LA	LA	LAKC			LAKC
Rb^+		LA		LA			
Cs^+		LAKC		LA			
NH_4^+	LA	LAKC	LAKC	LAKC	LA	LA	LA

[a] L = LDN; A = AgI; K = KLN; C = CuS.

AgI suspensions showed extreme variability of response to salt type and concentration. While the presence of the salts mostly increased the true supercooling, changes with salt concentration were quite erratic. The concentration of AgI used in these tests is approximately 10^3 times the solubility of AgI in water (Linke, 1965). The addition of halides will increase the solubility; most markedly so for the iodides. At 0.1 m KI and NaI all the AgI in the samples would be dissolved according to equilibrium data (Linke, 1965). This offers at least a partial explanation for the results; in particular the large increases in TS with 0.1 m KI, LiI, CsI and RbI support the suggestion. The lack of comparable changes with NaI and NH_4I and the reversal in trend with LiI at 1.0 m concentration indicate that either other factors than dissolution are also present or nonequilibrium conditions prevail. The ammonium salts were the only group with a common cation for which there is a fairly consistent decrease in true supercooling, but again the effect is not uniform with respect to concentration. The extreme sensitivity of AgI to the presence of ions demonstrates the ease with which the nucleating ability of AgI is influenced.

The KLN nucleant exhibited variations of true supercooling with concentration and salt type which were greater than those of LDN but, in general, not as great as those for AgI. The sample of 1.0 m LiI showed a remarkable decrease of 11.9°C in true supercooling ($\alpha = -11.9$°C). This was the only case of $\alpha < 0$ for KLN at high salt concentrations. Of the ammonium salts tested with KLN, all showed at least a slight decrease in true supercooling at some concentration.

Samples containing CuS showed variations with salt type and concentration similar to, but not as great as, the AgI samples. The NH_4I sample at 1.0 m LiI also showed a significant decrease, but not as great as for KLN. There is not much else that is noteworthy about the behavior of CuS.

Based on the results obtained with the four nucleants, at least a few generalizations are possible. All of the iodides caused at least some decrease in true supercooling; KI showed the smallest decrease. The two inactive nucleants (KLN and CuS) exhibited basically similar behavior: slight increases in true supercoolings with increasing salt concentrations. Changes in true supercoolings were typically less than 5°C at all solute concentrations. The patterns of increases and decreases for changing concentrations of a given salt were different for each nucleant; conversely, each salt produced a different pattern for a given nucleant, with the exception of LDN which on the whole was found to be inert to influences of dissolved ions.

In order to examine whether the magnitude of α for a given nucleus might depend in some systematic way on the original activity of the nucleus, tests were made in which the α-values were determined for individual drops. Three iodide salts (NaI, KI and NH_4I) were used for these tests. Indeed, a correlation was found: the least active nuclei underwent the greatest changes. This correlation is a manifestation of the fact that essentially all nuclei in a given suspension became equally effective in the solutions containing I^- ions, independent of the original effectiveness of the nuclei in pure water.

The time scale of the experiments also merits further comment. The time allowed in the tests for interaction of the nucleant with the solute ions was kept constant at about 10 minutes. Special experiments (to be presented elsewhere) have shown, at least for AgI, that the effects of solutes on nuclei depend on the time of interaction. For a number of iodide salts AgI exhibited an instantaneous (of the order of seconds) activation which subsequently decayed, the decay rate being different for different salts. Generalizing this observation means that the results presented in this paper have their primary value as comparisons, and that a more complete description would require determination of the magnitudes of the initial activation and of the decay rate for each nucleant-solute combination. These two quantities are indicated to be the fundamental characteristics of the interactions.

3. Discussion and conclusions

A profound influence of soluble salts on heterogeneous freezing nuclei has been demonstrated in these experiments. It has been shown that the effects are not simple and that dissolved salts may decrease or increase the activities of

hetero-nuclei. These changes in activity are superimposed onto melting point depressions caused by the salt solutions. So, while the basic information for assessing the results of the solute-nucleant interactions, and to thereby gain insight into the nature of the nucleating sites, is the "true supercooling", in atmospheric applications the relevant parameter remains the "apparent supercooling" (cf. Fig. 1).

The atmospheric relevance of the results is of particular interest. Of the salts tested, $(NH_4)_2SO_4$, NaCl and sea salt were most representative of natural CCN. Fig. 8 shows the observed true supercoolings as a function of salt concentration for LDN and KLN. Salt concentrations to be expected in cloud droplets can be readily reviewed with reference to Table 4. From this table it can be seen that droplets with salt concentrations exceeding 0.1 m would form rarely, since the number of particles >5 μm radius is quite low in the atmosphere. However, even the more numerous smaller particles (<1 μm radius) can lead to salt concentrations up to 0.1 m in cloud drops typical of many types of clouds. Fig. 8 shows the effects of soluble CCN below 0.1 m concentration to be either to decrease or to increase the activities of nuclei by a maximum of about ± 4°C.

A hetero-nucleus may be incorporated into a saline cloud drop by either one of two processes. First, an ice nucleus may be coated by or embedded in soluble material. Given a suitable environment, the soluble material will take up water and a cloud drop will grow. The

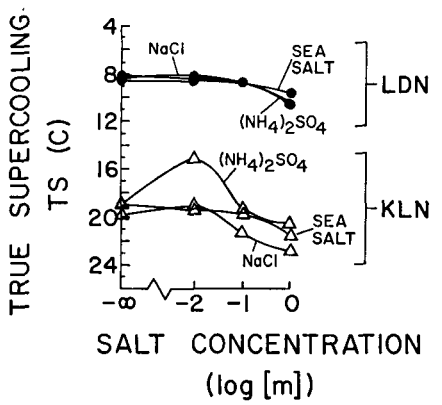

Fig. 8. True supercooling as a function of salt concentration for LDN and KLN hydrosols with $(NH_4)_2SO_4$, NaCl and sea salt.

Table 4. *Concentration (molality) of typical cloud droplets formed on NaCl particles of various sizes*

NaCl radius, μm	Droplet radius, μm	Molality of solution
0.1	5	3.1×10^{-4}
0.1	10	3.7×10^{-5}
0.1	20	4.6×10^{-6}
1.0	5	3.2×10^{-1}
1.0	10	3.7×10^{-2}
1.0	20	4.6×10^{-3}
5.0	10	5.1
5.0	20	5.1×10^{-1}

second process is the collision of an ice nucleus with a cloud drop.

In the first case, the ice nucleus would be initially surrounded by a highly saline environment. Under these conditions freezing nucleation will be hindered by the melting point depression, and either aided or retarded by the interaction of the salt with the nucleus, until the cloud droplet grows to sufficient size to reduce the salt concentrations. In addition, the high initial concentration of salt may impart irreversible effects to the nucleus. Some initial tests with $NH_4I + AgI$ combinations suggest that such irreversible effects are possible.

When an ice nucleus collides with an existing cloud drop, the drop may already have grown to a size sufficient to produce a dilute salt concentration. The results of the present study are perhaps most applicable for this case. The results for AgI and CuS might be taken as indicative of the behavior to be expected for artificial nuclei, while the results for LDN and KLN might be taken as representative of the effects of soluble salts on natural nuclei.

AgI is widely used in cold cloud modification programs. Dispersion of AgI particles involves the use of generators which burn acetone solutions of AgI dissolved with NaI, KI or NH_4I or the use of pyrotechnic mixtures. Products of generator systems using KI or NaI have been found to consist of complex salts of AgI and KI or NaI (Koenig, 1964; De Penna & Caimi, 1967). The soluble parts of these generator products were believed to decrease the activities of the AgI particles due to promoting condensation onto the particles and deactivation or dissolution of the AgI in the water (St.-Amand

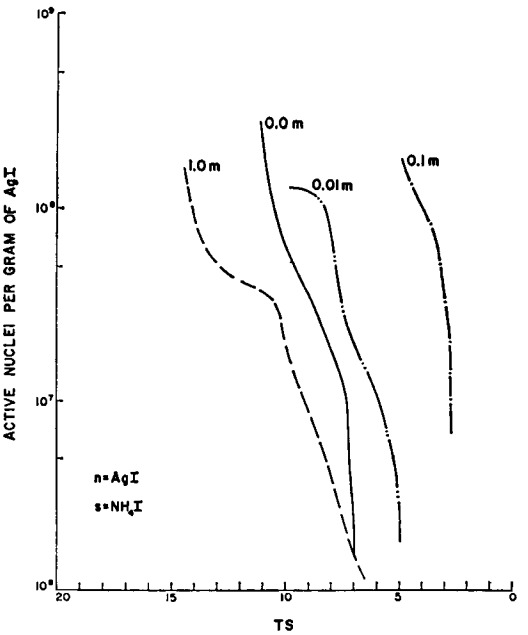

Fig. 9. Nucleus spectra of AgI hydrosols in 0.0, 0.01, 0.1 and 1.0 molal NH_4I.

et al., 1971). The present results add another consideration. Even if the AgI is not completely dissolved, KI and NaI will lower the activity of AgI at least for high concentrations. However, for short-time exposures of AgI to low concentrations of NaI or KI, increases in activity might be expected. Although NH_4I has not been definitely identified in the products of generators using this salt as the solubilizing agent, the possibility that trace amounts of NH_4I in fact are present cannot be discounted. The true supercooling of AgI hydrosols varies with NH_4I concentration. For example, the nucleus spectrum for AgI with 0.1 m NH_4I (see Fig. 9) reveals that the number of active nuclei per gram of AgI at -4°C is more than two orders of magnitude greater than without the NH_4I present. There have been reports indicating that generators using NH_4I–AgI solutions show greater activity at warm temperatures than do generators using KI or NaI (Zettlemoyer et al., 1963; Donnan & Blair, 1970; Henderson, 1972). Research aimed at determining if the observations reported for field generators are due in part to the effect reported in this work would be of importance.

Because the changes in true supercooling brought about by dissolved salts were found to be different for different hetero-nuclei, it is concluded that these changes result from modifications of the nucleating surfaces or from changes in the molecular arrangements at the interface and are not related in any simple way to modifications of the structure of the bulk liquid. It follows from this argument that the interactions ultimately depend on the ratio of nucleant surface areas to solute ion concentrations. Therefore, proportions different from those which existed in the present tests might be expected to lead to different results.

Since the observed temperature changes with varying salt concentrations were found to be different for each nucleus-salt combination, the opportunity exists to "fingerprint" natural nuclei, in precipitation for example. A series of tests with different salt solutions and at different concentrations might produce characteristic reactions (α-values) which, when compared to results obtained with known nucleants of different kinds, could reveal the composition of the natural nuclei. This information is not available at present from any other direct test of the nuclei themselves.

The main thrust of this work was to produce a survey of solute-nucleant interactions. The results, while certainly incomplete, nonetheless provide some appreciation for the range of modifications of nucleating ability that might result from dissolved salts in the water. It remains for future research to establish the physical mechanism responsible for the effects here reported.

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ЯДРА ЗАМЕРЗАНИЯ В ЖИДКИХ ЭЛЕКТРОЛИТАХ

Были выполнены эксперименты для определения размеров влияния присутствия растворенных в воде солей на нуклеационные способности искусственных и естественных ядер замерзания. С использованием техники замораживания капель было проверено 4 различных типа ядер замерзания (при фиксиро ванных концентрациях) в комбинациях с 10–20 растворимыми солями. Были определены изменения температур замерзания для каждой комбинации ядро — раствор соли при концентрациях соли 0, 0.01, 0.1 и 1 моль на литр. Были отмечены большие различия в реакциях разных ядер и был сделан вывод, что влияние растворенных солей на гетерогенную нуклеацию замерзания происходит не благодаря изменениям в общей структуре массы воды, но из-за модификации на поверхности раздела ядро–зародыш. Измерения указывают, что можно ожидать, что содержание солей в облачных каплях меняет нуклеационную активность взвешенных частиц в образовании льда вплоть до величины ± 4°C.