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The effect of water soluble salts on the nucleating ability of the AgI–AgBr–CuI system

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Experiments have been done to determine the extent to which the nucleating ability of 50:25:25 mol% composition of AgI, AgBr and CuI fusion material is influenced by the presence of soluble salts. Using a bulk freezing technique, the freezing nucleation temperatures are measured for each salt combination with the nucleant, at salt concentrations of 0.01, 0.1 and 0.5 M. For this, 21 soluble salts have been considered. These salts are found, in general, to increase the supercooling to varying amounts depending upon the salt type and the concentration. But NaCl, at 0.01 M concentration significantly improved the nucleation ability of the material and the nucleation temperature was found to be as high as −0.35° C. The combination of chlorides as well as some sulphates are found to exhibit a decrease in nucleation activity of the material.

1. Introduction

It is well known that the freezing process of water in the atmosphere always proceeds through the heterogeneous ice nucleation of supercooled water. Despite the fact that a large amount of laboratory and field work has been done in the last few decades to understand the phase change of water vapour and liquid water into ice crystals in the atmosphere, some of the basic features of this heterogeneous ice nucleation process still have not been clarified. In fact, experiments have shown that a good ice-forming nucleus is one that is relatively large and water-insoluble, has crystallographic properties similar to those of ice, and has at its surface emanating bonds that are similar to the O–H–O bond in ice [1].

Since natural cloud condensation nuclei 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 [2]. Moreover, during the process of weather modification by artificial ice nucleants, if the generator effluent contains considerable amounts of soluble materials, the ice nucleating properties of these seeding materials may be largely affected.

After testing the effect of a mixed solution of $MgCl_2$ and Na_2SO_4 on the nucleation threshold temperatures of AgI, hallosite, illite, montmorrillonite and kaolinite, Hoffer [3] found depression in the nucleation temperatures. Also, the depression was greatest for saturated solutions. Further, Evans [4] observed that the nucleation temperatures of phloroglucinal dihydrate were raised in NaCl solutions of varying concentrations. He even suggested that the increasing salt concentration induced two-dimensional crystallization of the monolayer.

Using a drop freezing technique, Reischel and Vali [2] examined the influence of about 10 to 20 soluble salts on the nucleating abilities of kaolinite, leaf derived nuclei, silver iodide and cupric sulphide. They reported that the salt contents of the cloud droplets can be expected to alter the ice nucleation ability of the suspended particles by as much as ± 4° C. In addition, the effects were found to be specific to each nucleant tested. Ramachandra Murty and Ramana Murty [5] found that the polarizability of the cations of the different soluble salts have greater impact to varying amounts on the ice nucleation temperatures of AgI. Recently Gobinathan and Ramasamy [6] studied the ice nucleating behaviour of PbI_2 in the presence of some soluble salts. They found that among the various iodides tested, NH_4I remarkably increased the nucleation activity of PbI_2 by about 2° C.

In the present study, we have examined independently the influence of 21 soluble salts on the ice nucleation activity of the AgI–AgBr–CuI system, for the first time. In our previous paper [7], we have reported that the 50:25:25 mol% composition of AgI, AgBr and CuI has the lowest misfit with ice (0.0532%) and hence the highest nucleation temperature (− 0.48° C). As it was rightly pointed out [2], a need was felt to evaluate the solute effects on this specific AgI–AgBr–CuI nucleant so that the ambiguity, whether the observed facts in the past are due to modifications of the structure of water, changes of activity of nucleating particles or the inadvertant additions of nuclei with the soluble salts, could be removed. Hence, the present investigation.

2. Experimental details

2.1. Preparation of the samples

The preparation of AgI–AgBr–CuI samples of various molar compositions by the method of vacuum fusion has been explained elsewhere [7]. It was thought apt to choose those soluble materials which form the bulk of the soluble compounds in natural aerosols for use as soluble salts. Alkali halides were chosen, since

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these include a number of components of sea salt, which is one of the main sources of hygroscopic aerosols. In addition, the halides of lithium, the sulphates of sodium, potassium, ammonium, and magnesium, and $MgCl_2$ were considered. In fact ammonium sulphate is found to be invariably present in natural aerosols [8]. There is also definite evidence to show the presence of magnesium sulphate [9]. Analytical reagent (AR) grade purity salts were used as-received from the manufacturer.

The fusion sample of 50 : 25 : 25 mol % composition of AgI, AgBr and CuI was first ground to fine powder with an agate mortar and pestle. It was then carefully sieved into uniform sized particles (50 μm) using stainless steel meshes. Salt solutions of 0.01, 0.1 and 0.5 M concentrations were prepared first by weighing appropriate amounts of salt and mixing it in triple distilled water and then carefully filtered with Grade 1 Watman filter paper.

2.2. Ice nucleation studies

The method employed for the measurement of the nucleation temperatures was the same as detailed elsewhere [7, 10, 11]. Immediately before the experiment, 100 mg of the sieved sample was suspended in 100 ml of the filtered salt solution and stirred well. About 0.25 ml of it was placed in 20 similar test tubes and they were closed air-tight. Five of them were then introduced into a vigorously stirred cooling bath, for a single run. The bath was cooled at a rate of $0.1^\circ \mathrm{C\,min^{-1}}$. On visual observation of the emerging ice crystals, the freezing temperature was measured with a Beckmann thermometer with an accuracy of 0.01° C. Four runs were made for each concentration of a "salt" and hence, each nucleation temperature was the median of 20 observations with a fluctuation of $\pm 0.2^\circ$ C. The experiment was repeated and the mean of the two readings was taken.

Out of curiosity as well as to have the laboratory conditions to be more realistic with those that exist in the atmosphere, the authors have also experimented the combined effects of (i) NaCl, KCl and NH_4Cl (ii) NaCl, KCl, NH_4Cl and $MgCl_2$ and (iii) the sulphates of Na, NH_4 and Mg at salt concentrations of 0.01 and 0.1 M with the nucleant. Extreme care was taken to maintain a constant time scale for the experiments, without which a meaningful comparison and interpretation of the experimental data may not be possible. So, the time allowed in the tests for the interaction of the nucleant with the solute ions was kept constant at about 10 min. It is to be mentioned that this is the minimum period required for commencing the experiment after a suspension is prepared. This procedure was uniformly adopted throughout the investigation. Thus, the freezing temperatures were determined for each nucleant-salt combination at salt concentrations of 0.01, 0.1 and 0.5 M, in dust free air-conditioned room.

3. Results

The influence of the different salts on the nucleation activity of the 50 : 25 : 25 combination of AgI, AgBr and CuI fusion nucleant and the results of the measurements are represented in Figs 1 to 6. The freezing temperature of the nucleant in triple distilled water is determined to be -0.48° C. Among the halides tested in this study, the chlorides gave the best performance with the nucleant at 0.01 M concentration. As a matter of fact, NaCl at 0.01 M concentration has remarkably improved the nucleation activity of the nucleant so that the nucleation temperature was as high as -0.35° C (Fig. 1).

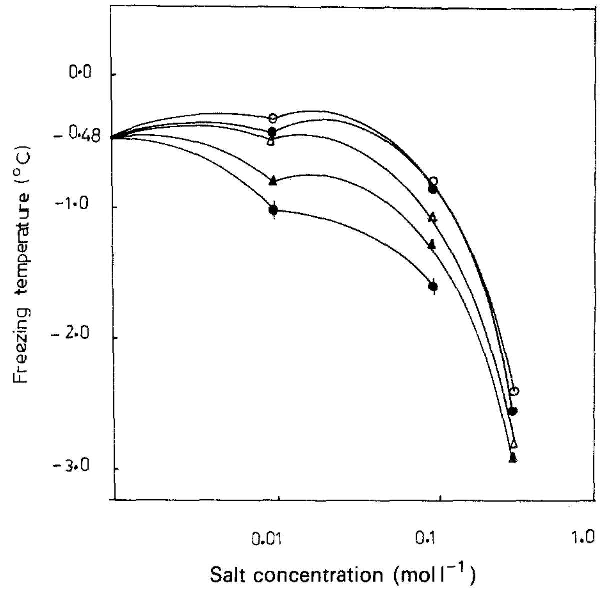

Figure 1 Freezing temperature as a function of salt concentration of the chlorides of Na, K, NH_4, Li and Mg with the AgI–AgBr–CuI fusion nucleant. (○) NaCl, (●) KCl, (△) NH_4Cl, (▲)LiCl and (●) $MgCl_2$.

The fluorides at 0.01 M concentration have exhibited basically similar behaviour. They have produced more or less the same effect and the supercooling is around -1° C, irrespective of the nature of the salt. All the bromides have exhibited larger supercoolings at all concentrations. So, the nucleation activity of the material has been largely reduced. Among the iodides, NaI and NH_4I have caused very small supercoolings at 0.01 M concentration whereas KI, at the same concentration,

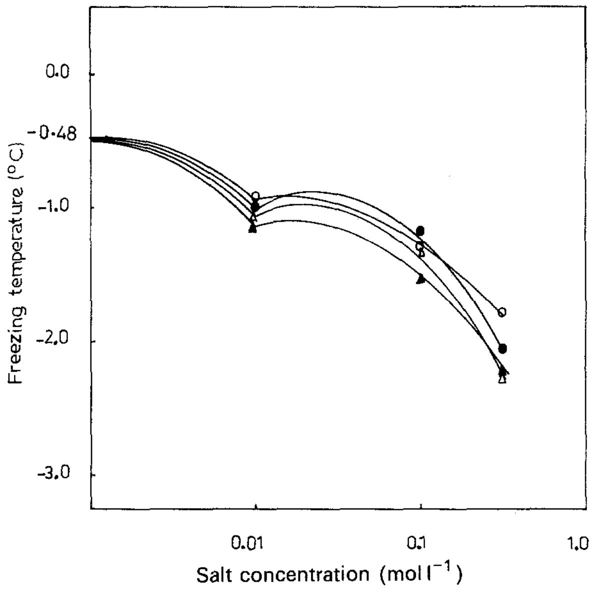

Figure 2 Freezing temperature as a function of salt concentration of the fluorides of Na, K, NH_4 and Li with the AgI–AgBr–CuI fusion nucleant. (○) NaF, (●) KF, (△) NH_4F and (▲) LiF.

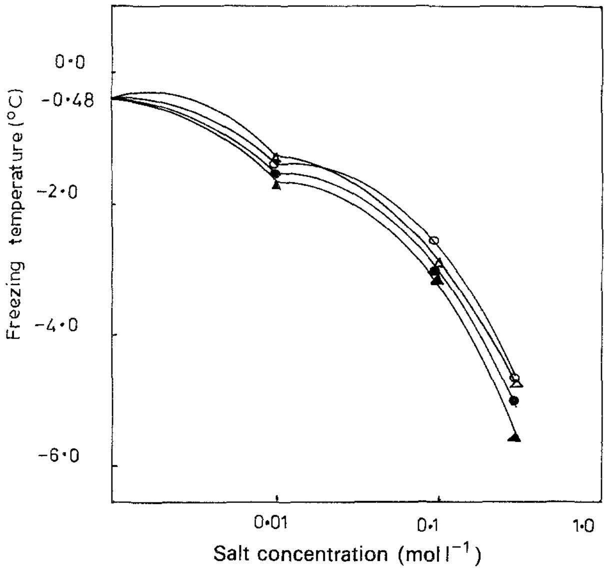

Figure 3 Freezing temperature as a function of salt concentration of the bromides of Na, K, NH_4 and Li with the AgI–AgBr–CuI fusion nucleant. (○) NaBr, (●) KBr, (△) NH_4Br and (▲) LiBr.

has surprisingly produced a greater supercooling. A further increase in the concentration of the iodides reduced the nucleation activity considerably.

All the sulphates examined have shown lesser supercooling than the bromides and hence a slight decrease in the activity of the system. The variations in nucleation temperatures are also small. It is rather surprising to note that the combined effect of NaCl, KCl and NH_4Cl on the nucleant at 0.01 M concentration. Their individual influence in increasing the nucleating capacity of the nucleant has been totally reversed to produce a supercooling of −0.6° C, when they are combined. This reduction in activity is further increased by the addition of $MgCl_2$ with the above combination of salts at the same concentration. Similarly, the net effect of Na_2SO_4, $MgSO_4$ and $(NH_4)_2SO_4$ at 0.01 M salt concentration is found to have a greater increase in supercooling than the effects due to individual salts. Such behaviour also seems to be unique in both the cases at 0.1 M concentration.

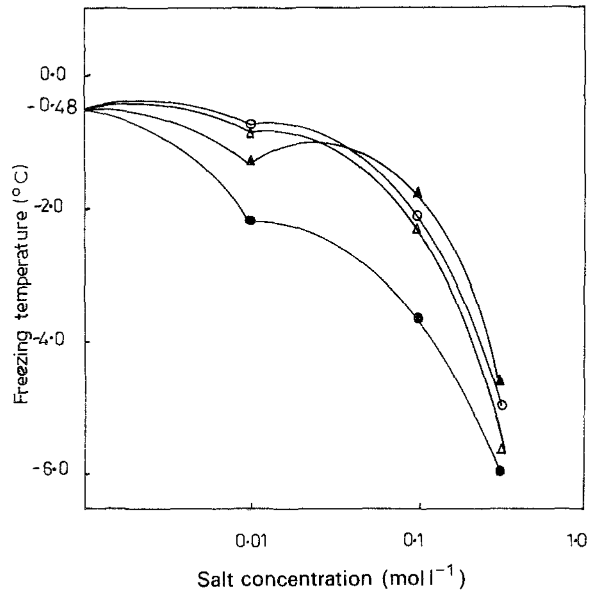

Figure 4 Freezing temperature as a function of salt concentration of the iodides of Na, K, NH_4, and Li with the AgI–AgBr–CuI fusion nucleant. (○) NaI, (●) KI, (△) NH_4I and (▲) LiI.

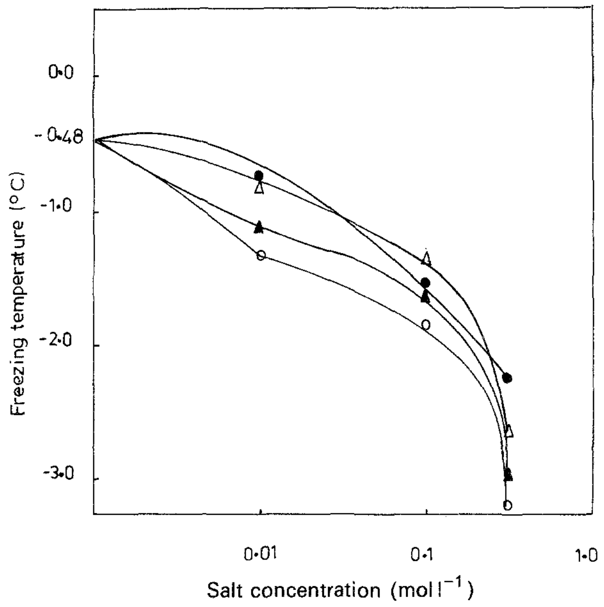

Figure 5 Freezing temperature as a function of salt concentration of the sulphates of Na, K, NH_4 and Mg with the AgI–AgBr–CuI fusion nucleant. (○) Na_2SO_4, (●) K_2SO_4, (△) $(NH_4)_2SO_4$ and (▲) $MgSO_4$.

4. Discussion

It is found that the size of the nucleant particle plays an important role in the determination of its nucleation temperature [12, 13]. Hence, uniform sized particles (50 μm) have been used throughout this study.

It is reported [14] that large quantities of water-insoluble particles were found to be present in the solution with the solute even though high purity, AR grade salts were used. To remove as many particles as possible, the solutions were filtered through Grade 1 Watman filter paper. Further, all the solutions were tested prior to their use in mixture with the nucleant.

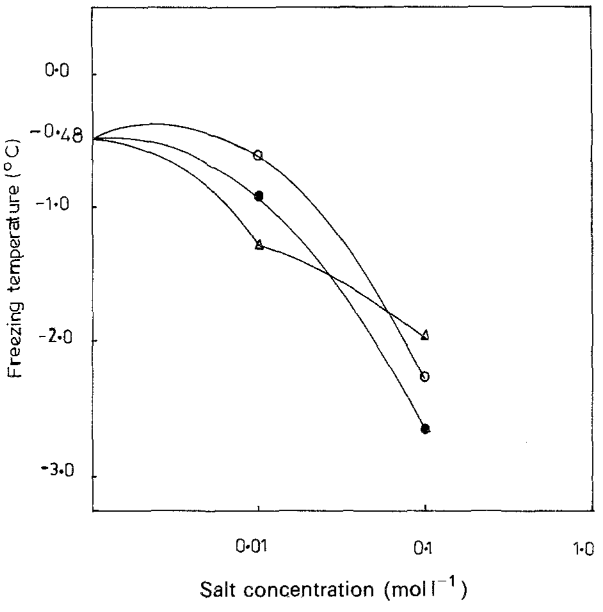

Figure 6 Freezing temperature as a function of salt concentration of the combination of (i) chloride salts and (ii) sulphate salts with AgI–AgBr–CuI fusion nucleant. (○) [NaCl + KCl + NH_4Cl], (●) (NaCl + KCl + NH_4Cl + $MgCl_2$], (△) [Na_2SO_4 + $(NH_4)_2SO_4$ + $MgSO_4$].

The nucleation temperatures were found to be sufficiently low to ensure that the nucleus concentration was low.

It is quite evident that the bulk of a particular type of a solution did not freeze at a single temperature but over a range of temperatures. Therefore, the median of 20 observations with an uncertainty of $\pm 0.2^\circ$ C was taken to be the nucleation temperature in each nucleant–salt combination of each concentration. Since the salt solutions in distilled water resembled the type of cloud droplets in equilibrium with the natural atmosphere, the measured nucleation temperatures of the salt solutions at different salt concentrations with the nucleant also have some interesting results.

From Figs 1 to 6, it is clear that AgI–AgBr–CuI nucleant suspensions have shown extreme variability of response to salt-type and concentration. The presence of salts, in general, has increased the supercoolings but at the same time exceptions are not rare and are of special interest.

Among the chlorides (Fig. 1), only NaCl and KCl at 0.01 M concentration have exhibited increased nucleation activity of the nucleant. Especially, NaCl showed an excellent performance with the nucleant, producing the highest nucleation temperature of -0.35° C. But some reports from literature [15–18] have mentioned that NaCl mostly favours greater supercooling with the nucleants, so far tested. In order to confirm the result obtained with the present nucleant, the experiment with NaCl alone (0.01 M) was repeated five times and the readings were encouragingly found to be consistent. Even at 0.1 M concentration NaCl, KCl and NH_4Cl did not have any appreciable supercoolings whereas LiCl and $MgCl_2$ were found to be associated with greater supercoolings.

The possible reasons for such behaviour of chlorides can be explained as follows. It is an established fact that when electrolytes are dissolved in water, they are partly or fully dissociated into ions. Due to the interaction between the electric field of the ions and the electric dipole of the water molecules, water molecules are turned out of the ice-like structure. In this way, bonds between the oriented molecules and the neighbouring molecules are broken [14]. Breaking of the water structure also takes place because most of the ions do not fit perfectly into the water structure. Hence, the water lattice is either expanded or contracted by means of the electric forces of the ions. Thus the disruption of the water lattice and the breaking of the bonds cause an increased number of vacant lattice sites and interstitial molecules. Moreover, molecular shape and size are important for the activity of the potential ice nuclei and in the formation of surfaces where the density of the hydrogen bonding groups is high. The flexibility of hydrogen bonding groups and of the crystal lattice may further help to reduce the strain energy for embryo formation [19]. In order that an ice nucleus of critical embryo be formed in supercooled water, ice-like clusters have to be formed among the water molecules. But, when the water lattice is more disrupted and more bonds are broken, the formation of such a cluster becomes very difficult.

It is true that the larger the size of the ion, the greater is the polarizability which, in turn, causes a greater structure-breaking effect. The ionic radii of Na^+, K^+, NH_4^+, Li^+ and Mg^{++} are 0.097, 0.133, 0.143, 0.068 and 0.066 nm, respectively. Since the Na^+ ion is smaller than the K^+ ion and the NH_4^+ ion, the structure breaking effect of the Na^+ ion is very small. Similarly, the structure breaking effect of the K^+ ion is smaller than that due to the NH_4^+ ion. A greater structure-breaking effect will ultimately lower the nucleation activity or ice formation will become less probable. Our experimental findings fully support this statement at the higher concentrations of 0.01 and 0.5 M. It is found that at 0.01 M concentration, NaCl and KCl have improved the nucleation activity of the nucleant. The structure-breaking effect may, perhaps, be the least, in these cases.

Though Li^+ and Mg^{++} ions are both smaller than the Na^+ ion, they cause greater supercoolings at all concentrations. This behaviour is due to the process of hydration. It is well known that the smaller the ion, the greater is its hydration, during which process, a greater enthalpy of energy will be released. So, in the case of such substances, the process of hydration, which sets in after the crystallite comes into contact with water, continues until saturation is reached. It is rapid to start with, but slows down subsequently. This characteristic of hydration is attributable to the diffusion of water molecules into the interior of the crystallite, which is invariably time-dependent and which reaches saturation finally [20, 21]. As a result, the aggregation of water molecules which facilitates ice-formation, will be fast in the beginning, slow down thereafter and finally cease. The decrease noticed in the nucleation activity in the case of LiCl and $MgCl_2$ is a clear case of experimental evidence. Since Mg^{++} ion has two units of positive charge as well as smaller radius than the Li^+ ion, $MgCl_2$ has produced more supercooling than LiCl.

The fluorides (Fig. 2) have exhibited a smaller supercooling effect at 0.01 M concentration. When the concentration is further increased, the supercooling is also found to increase. This is readily expected because any dissolved substance will lower the freezing nucleation temperature, more so at higher than lower concentrations. But the problem does not end here. On carefully comparing the end results produced by the chlorides and the fluorides on the nucleant activity, one could easily note the following: that is, in both the cases (Figs 1 and 2), the cations are the same but the anions are different. The smaller F^- ion (0.133 nm radius) has reduced the nucleation activity at all concentrations whereas the larger Cl^- ion (0.181 nm radius) has caused a smaller supercooling effect. This is due to the fact that the smaller F^- ion is more hydrated, in which case a larger enthalpy of energy is released. This release of energy may ultimately hinder the ice-formation. Hence the fluorides produce more supercooling than the chlorides.

In the case of bromides (Fig. 3), the nucleation activity has been largely reduced at all concentrations. As the Br^- ion is comparatively larger (0.196 nm radius) than the Cl^- and F^- ions, and the cations being the same, the disruption produced in the water lattice is larger. This would necessarily be responsible for the greater supercoolings. This is in accordance with our experimental observations.

It is observed (Fig. 4) that the freezing temperatures of the AgI–AgBr–CuI system have been differently affected by the presence of different iodides. Ice formation on the adsorbed solute nucleating substrate depends on the aggregation of water molecules. The extent to which aggregation of water molecules takes place around the adsorbed ion depends upon the polarizability of that ion, its electronic configuration and the polarizing power of the oppositely charged ion in the pair. Weyl stated [22] that a liquid surface consists of the most polarizable ions because polarizability permits an adjustment of the force fields of the surface ions, as a result, a lowering of the surface free energy. Since this surface free energy is a function of the polarizability of the ions, the presence of more polarizable ions or molecules on the substrate will reduce the amount of supercooling, a favourable condition to form ice crystals. Therefore, it is expected that the nucleating activity of the present nucleant will be affected differently by the different iodides, depending upon the polarizing powers of the cations. As such, the polarizing powers of the cations Li^+, Na^+, K^+ and NH_4^+, decrease in order. Consequently, the nucleation capacity of the AgI–AgBr–CuI nucleus has to progressively decrease from Li^+ to NH_4^+ ions. This is found to be true at 0.1 and 0.5 M concentrations of the iodides except KI, which has exhibited very high supercooling. At 0.01 M concentration too, KI behaves in the same fashion and LiI has abruptly shown a reverse trend. Such behaviour is not quite uncommon and it is the characteristic of the iodides as has been observed with other nucleants such as AgI, in some of the earlier works [2, 23, 24]. AgI is widely used in cold cloud modification programmes. The products of generator systems using KI or NaI have been found to consist of complex salts of AgI and KI or NaI [25, 26]. The soluble parts of these generator products were believed to decrease the nucleation activities of the AgI particles. Similar processes are also expected to happen with the present nucleant. Another possible reason for the large supercooling effect due to the presence of KI may be due to its high ionic character.

All the sulphates (Fig. 5) have shown a lower supercooling effect at all concentrations than the bromides, and the results are also more interesting. Though the size of the Na^+ ion is smaller than the K^+ ion, the Na^+ ion has a hydration capacity to form $2Na^+(10\,H_2O)$-SO_4^{2-}, the decca-hydrate. But K_2SO_4 being anhydrous, the K^+ ion does not have any water molecules attached to it for hydration. Hence, structure breaking effect due to Na^+ ion is more severe than that due to K^+ ion. Such a situation would warrant larger supercooling with Na_2SO_4. Similarly, $(NH_4)_2SO_4$ is also anhydrous and so it has no water molecules for hydration. At the same time, the NH_4^+ ion is larger than the K^+ ion. On account of this, $(NH_4)_2SO_4$ would be expected to exhibit a slightly greater supercooling than K_2SO_4. Further, the Mg^{++} ion has seven water molecules ($7\,H_2O$) to form $Mg^{2+}(7\,H_2O)SO_4^{2-}$. Since it shows less hydration ($7\,H_2O$) than the Na^+ ion ($10\,H_2O$), the supercooling produced by $MgSO_4$ would be less than that due to Na_2SO_4, but greater than that due to the K_2SO_4 and $(NH_4)_2SO_4$ salts. All these are found to be true in this investigation.

The individual influence of NaCl on the nucleation activity of the system at 0.01 M concentration was appreciable (Fig. 1). But such a remarkable activity of NaCl has been reversed when it is combined with KCl and NH_4Cl (Fig. 6). This reduction in activity has been further increased when $MgCl_2$ is added to the above combination, at the same concentration of 0.01 M. However, the supercooling produced by the combination of these four salts is actually less than due to $MgCl_2$ alone. A further increase in the concentration of the salts to 0.1 M causes a large supercooling. The combination of the sulphates of Na, NH_4 and Mg at 0.01 and 0.1 M concentrations is also found to exhibit more supercooling with the nucleant.

5. Conclusion

It is found that the presence of soluble salts has reduced the ice-forming ability of the material, chosen in this study. All the bromides have exhibited greater supercooling than any other halides or even the sulphates at all concentrations. NaCl, at 0.01 M concentration has improved the nucleation activity markedly. To a first approximation, taking the salt concentration present in the natural aerosols to be a maximum of 0.01 M, the combined effects of chlorides of sodium, potassium, ammonium and magnesium as well as the sulphates of sodium, ammonium and magnesium are found to produce more supercooling.

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