ICE NUCLEATING BEHAVIOUR OF AQUEOUS AND ALCOHOLIC SOLUTION OF PHLOROGLUCINOL: A LABORATORY STUDY

S. Paul, A. Hazra, D. Roy, U. K. De,
Atmospheric Science Research Group
M.Phil Programme in Environmental science
Faculty of Science, Jadavpur University

S. Bhar
Dept. of Chemistry
Jadavpur University
Kolkata 700 032, India

K. Goswami
Dept. of Physics
Jadavpur University
Kolkata, 700 032, India

Abstract: The behaviour of ice nucleation at different temperatures has been studied in case of seeding with aqueous solution and alcoholic solution of Phloroglucinol. For aqueous solution, the nucleation has been studied starting from -17.9^0C and it was observed to terminate at -0.5^0C. In case of alcoholic solution, the study has been started from -22.3^0C and it was found to continue up to -3.5^0 C. The higher temperature is a cut-off temperature, but at the lower temperature end the nucleation becomes quite small, though not amounting to zero. However the peak in crystallization occurs at -13.0^0 C in the case of aqueous solution and the corresponding peak occurs at -17.8^0 C in the case of alcoholic solution. Apparently both these temperatures are close to the freezing temperature of the mixture.

Besides, dendrite structure is observed in both the cases in the temperature range of -20^0C to -17^0C. However, hexagonal crystals have only been observed in case of aqueous solution in the temperature range of $-15\ ^0$ C to $-10\ ^0$ C. Cubic crystals exist dominantly in case of alcoholic solution, but rod shape crystals dominate in case of aqueous solution.

1. INTRODUCTION

The study of ice nucleation by organic substances started from late fifties of the last century. Some of these which are reported in the literature may be mentioned here (Baskirova & Krasikov 1957, Komabayshi & Ikebe 1961, Head 1961,1962, Langer & Rosinki 1963, Fukuta 1963,1965,1966, Braham 1963, Parungo & Lodge 1965,1967, Fletcher 1972, Michelmore & Franks 1982, Gravish et. at. 1990, 1992, Hendrick & Ward 1992, Pattnaik et. al. 1997, Szyrmer & Zawadzki 1997).

In fact, Bashkirova and Krasikov (1957) were the first persons to identify Phloroglucinol as an efficient ice nucleant. During 1961-62, Langer & Rosinski were engaged in an Air Force sponsored study of basic characteristics of organic crystals as ice nucleant. Of more than 30 compounds studied by them in the laboratory (Langer & Rosinski, 1963), Phloroglucinol turned out to be most promising as ice nucleant. They conducted test in Armour Research Laboratory and found that Phloroglucinol dust can cause rapid nucleation in cold box cloud at the temperatures of -2^0 C to -3^0 C.

In 1963 Braham also identified Phloroglucinol as an ice nucleating substance. This group performed mainly field experiments. They released Phloroglucinol at different temperatures in the environment. They recorded a moderate snow shower (at -17.2^0C) at the ground and reported that the heaviest shower had occurred at -9.8^0C. Besides, they observed that dispersed Phloroglucinol had the ability to induce freezing of small droplets close to 0^0 C but on the negative side.

Some further experiments were carried out by Langer et. al. (1978) with the same substance. They used Phloroglucinol dust and observed that when the diameter size was in the range $0.04\text{x}10^{-6}$m to $0.06\text{x}10^{-6}$m, the dust particles acted as good cloud condensation nuclei. On the other hand, when the diameter size was reduced in the range of 0.02 $\text{x}10^{-6}$ m to 0.03 $\text{x}10^{-6}$ m, these served as ice nucleating agent.

In a more recent field experiment in Phillipines (Valeroso & Santos, 1999), alcoholic solution of Phloroglucinol was sprayed in a developing cumulus cloud in a region where temperature was close to 0^0C. Heavy rainfall was observed to occur almost 18 minutes after the seeding.

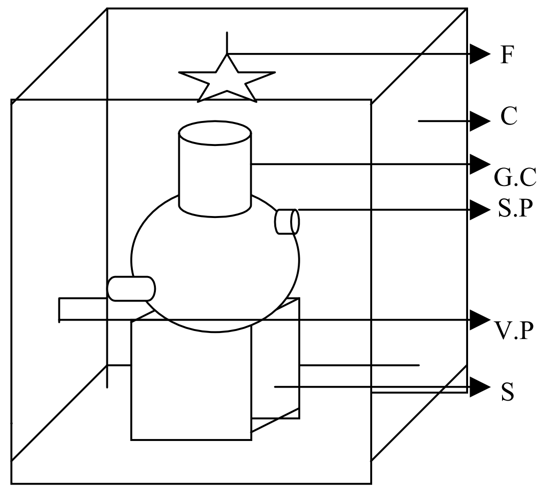
In fact, Phloroglucinol can be seeded in three forms i.e. as dust, as aqueous solution and as alcoholic solution. In case of dust, the nucleation depends on the size of dust particles, on the amount of dust seeded and lastly on temperature. Since the size of the dust particles can be varied over a wide range, it needs an exhaustive study. Here, only the alcoholic solution and the aqueous solution of Phloroglucinol have been used as seeding agent and the behaviour as ice nucleant over a wide range of temperature has been studied systematically. The entire experiment has been operated in a Cold Room. Firstly, the seeding temperature was systematically varied and the crystal count was made, keeping concentration of seeding material fixed. The same experiment was done for both the solutions. It can be concluded that some new results have come out from the present study.

2. EXPERIMENTAL APPARATUS & MEASUREMENT TECHNIQUE

The experimental work has been done inside a single door metallic room (Cold Room) with refrigerant lining and the dimensions of the room are as follows.

The length, breadth, and height are 1.52 m, 1.52 m, and 1.83 m respectively (Diagram 1). The room is made of galvanized iron sheet and is insulated by PUF. The temperature of the room can be reduced up to -35^{0}C. One thermistor is placed inside the Cold Room and this measures the temperature inside the room. A digital display shows the temperature. An air conditioner is operated outside the Cold Room to decrease the temperature difference between inside and outside of the Cold Room. Another thermistor measures the outside temperature and the temperature is displayed digitally. Inside the Cold Room a spherical glass vessel of 35.6 cm diameter and 20 liter volume is placed and it has several outlets on its body for different purposes. A cloud of supercooled droplets is produced by cooling the chamber and then passing steam through a hole near the floor of the chamber. To produce steam a closed container with water has been used, which is placed on a heater and steam is passed inside the vessel through a pipeline. The amount of water vapor content inside the vessel is controlled by adjusting the steam flow. There exists one seeding port on the body of the vessel through which the seeding material is injected. Two thermistors are used to measure the temperature inside the vessel where the seeding experiment is done. Of the two thermistors, one is kept just above the seeding port and the other is placed near the floor of the vessel. The seeding temperature being mentioned in the literature is actually the temperature observed from the sensor just above the seeding port as the nucleation mostly occurs around that region. The other sensor is used mainly to check if there is any temperature gradient inside the chamber. Both these sensors provide digital display. It should be mentioned that all the thermistors are calibrated at ice and steam points and the calibration error lies within 0.1^0 C. Also the temperature difference between the two sensors within the vessel never goes beyond 0.1 ^{0} C.

One circulator is fixed at the roof of the Cold Room to keep the temperature uniform inside the Cold Room as well as to circulate the water vapour. A light is also kept for working purposes inside the Cold Room.



(C= Cold Room, S.P.= Seeding Port, V.P.= Vapor Port, G.C.= Glass Chamber, S= Stand, F= Fan)

Diagram-1: Schematic Diagram of Cold Room

To collect the ice crystals, formvar coated slides are used. Formvar is a brand name of Polyvinyl Formal Resin. The slide acts here as a replicator. By taking 0.4 gm of formvar in 10 C.C. of chloroform a solution is made which is coated on the slides. Two formvar coated slides are placed on a tray near the floor of the spherical vessel to collect the crystal signature. When the slides are taken out, chloroform quickly evaporates leaving behind a plastic film of formvar. On the other hand, ice part of the crystal is also converted into water. Then the slides are kept inside a desiccator with sufficient silica gel so that water will evaporate and be quickly absorbed by silica gel. By this process a replica of the arrested crystals is retained and also the nucleating agent at the core in case of heterogeneous nucleation is left behind. The use of formvar for the purpose of replication is already documented (Saunders & Wahab 1973, Hallet 1976 a,b).

Though two types of seeding solution have been used, one is aqueous Phloroglucinol solution and the other is alcoholic Phloroglucinol solution, but in both the cases the concentration is kept at 0.25 gm of Phloroglucinol in 25 c.c. of either solvent. Only 0.5 c.c. of the solution is injected in one stroke with the help of an atomizer and the atomizer can produce droplets of size 0.4μm to 1.0μm with the maximum number at 0.7μm and the standard deviation being 0.21μm.

The replicators are removed from the vessel after 2 minutes of stoppage of the seeding operation. The slides are then kept inside a desiccator to dry. After the drying up of the slides, these are viewed with the help of a microscope. The microscope has 400 times magnification and the number of crystals in a field of view of the microscope is counted. The basic habit of crystals with change of temperature is also investigated. Photomicrography of those crystals has been done with the help of a camera attached to the microscope.

3. EXPERIMENTAL RESULTS

In the present work, the comparative ice nucleating property of aqueous solution and alcoholic solution of Phloroglucinol has been studied.

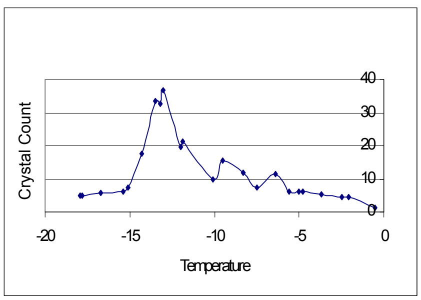


Fig-1: Crystal Count against Seeding Temperature in case of Aqueous Solution of Phloroglucinol

Phloroglucinol is moderately soluble in water, but its solubility largely increases in alcohol. In fact the dipole interaction between water and Phloroglucinol is much greater than that with Ethyl Alcohol, but it is evident that non-ionic weak interaction prevails in case of alcoholic solution.

One of the major aims of the present work is to examine how the crystal count changes with change of temperature at a definite Total Water Content (TWC). However, TWC could not be kept totally fixed but attempts were made to contain it within a range of 130 gm to 150 gm. In the present experiment two slides were kept at a time in the chamber. In each slide, ten fields of view were considered for counting. Then, at each temperature, four separate observations were taken. So, the average of 80 observations of crystal count is being presented here. In Fig.1, the variation of crystal count with seeding temperature in case of seeding of aqueous solution of Phloroglucinol is presented. Here, the most dominant peak in crystal count occurs at -13^0C. So, this temperature is most suitable for ice nucleation by aqueous solution of Phloroglucinol. It is also observed that the upper cut-off of ice nucleation occurs at -0.5^0C. In the lower temperature range, the observation has been continued up to -17.9^0C where nucleation becomes small, though it does not vanish. It should be noted that -12.0^0C is the eutectic temperature for Phloroglucinol and water mixture (this is observed experimentally). As reported in many other cases (Knollenberg, 1966; Hazra et. al., 2003) there is a common tendency for freezing at eutectic temperature as Gibb's free energy becomes minimum at that temperature (Azaroff, 1995). So the peak in number count observed at -13.0^0 C may be taken due to that usual tendency.

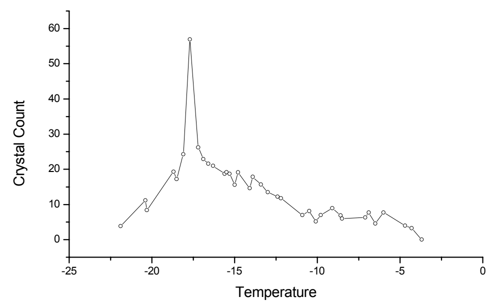


Fig-2: Crystal Count against Seeding Temperature in case of Alcoholic Solution of Pholoroglucinol.

In case of study of ice nucleation by alcoholic solution of Phloroglucinol, the amount of seeded material as well as its concentration are kept the same as previous case, as mentioned previously. The variation of number count of crystals with change of temperature is presented in figure-2. A sharp peak in number count is observed at -17.8^0C. There is a higher temperature cut-off at $-3.5\ ^0$C. The observation at lower temperature was continued up to $-22.3\ ^0$C and the nucleation did not totally cease there.

It should be noted that in case of alcoholic solution of Phloroguconol in contact with supercooled droplets, three different interfaces are involved. One needs to consider the condensation of the three media together. However, in what ratio the three media will condense in the present environment that cannot be clearly judged. As the amount of alcoholic solution of Phloroglucinol is small in aqueous environment, a study has been conducted in the laboratory to find the freezing temperature of the mixture by varying the ratio of alcoholic solution of Phloroglucinol and liquid water (Fig.-3). It is observed that when 30 cc of alcoholic solution of Phloroglucinol is in combination with 100 cc of liquid water, the entire amount freezes exactly at temperature at -17.8^0C. So one can again conclude that the peak in crystal count occurs where the three body mixture can freeze together.

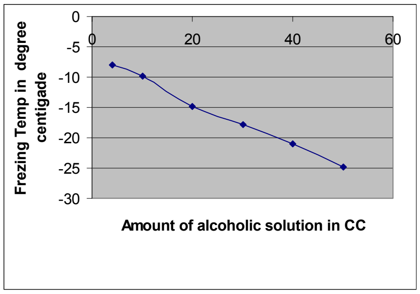


Fig-3: Freezing Temperature against Amount (CC) of Alcoholic Solution used with 100 CC of Water .

From Fig.- 1 and Fig.-2, it is clear that at the peak of nucleation, the alcoholic solution of Phloroglucinol is more efficient as ice nucleant than the aquatic solution of Phloroglucinol.

Some remarkable morphological features in ice crystal formation have been detected in both the cases. One of the distinctions between the two is the existence of hexagonal crystals in case of aqueous solution, in the temperature range of $-15\ ^0$C to $-10\ ^0$C; it should be mentioned that no hexagonal crystal has been observed in case of alcoholic solution. It should also be stressed that nice dendrites (ref. Photo 001,002) are observed in both the cases in the temperature range of -20^0C to -17^0C. Besides, dominantly cubic crystals are observed in case of alcoholic solution (ref. Photo 003,004) and in case of aqueous solution the rod shape crystals are more dominant(ref. Photo 005,006,007). Rod shape crystals observed in case of alcoholic solution are also being presented (ref. Photo 008).

4. CONCLUSION

Phloroglucinol may be considered as a seeding agent in three different forms at least. Already scientists have used Phloroglucinol as dust, as aqueous solution and then as alcoholic solution. It has already been reported in the literature that the nature of nucleation greatly depends on the size of the dust. As the detailed study of the character of the dust particles as condensation nuclei will involve exhaustive work, that attempt has not been made in the present study.

But the well known two solutions of Phloroglucinol as ice-nucleating agent have been utilized. In the present case, only a particular concentration of either solution has been seeded. One can also vary the concentration and examine whether the nucleation character has any variation.

One can conclude from the present study that the alcoholic solution of Phloroglucinol is more efficient for ice nucleation at the peak condition. Besides, the peak in ice nucleation in either case apparently occurs where the media have tendency to freeze together.

5. ACKNOWLEDGEMENT

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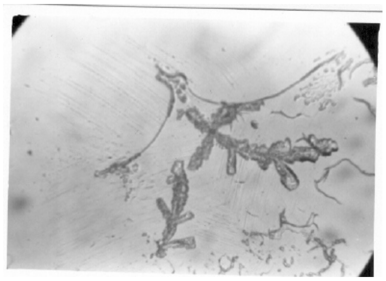
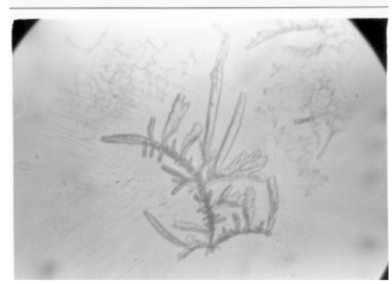
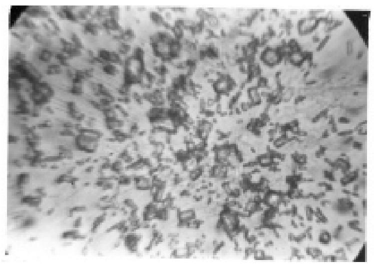


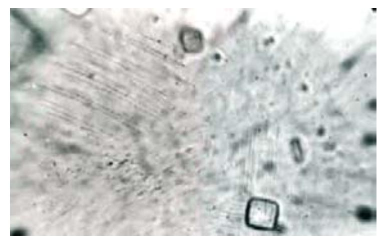
001:*Dendrite structure formed for aqueous Phloroglucinol at –17.9^0*



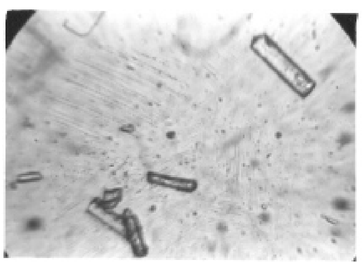
002*: Dendrite Structure formed in alcoholic Phloroglucinol at –20.4 ^{0} C.*



003*:Dense Crystal found for alcoholic Phloroglucinol at -17.7^{0}C.*

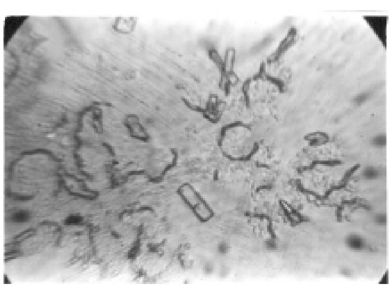


004*:Cubic crystal found in alcoholic Phloroglucinol -8.6^{0}C*

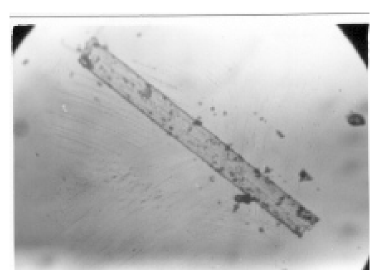


005*:Rod Shape Structure Found in Aqueous Phloroglucinol –10.1^{0}C*

006: *Rod shape structure formed for aqueous Phloroglucinol –8.3^{0}C.*



007*:Rod Shape and hexagonal crystal found in aqueous Phloroglucinol at –13.5^{0}C.*



008: *Nice rod shape found for alcoholic Phloroglucinol at –14.1^0 C.*