

A Study of the Effect of Size on Ice Nucleation in the Aerodynamic Range of Particles

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(Manuscript received 25 November 1981, in final form 31 March 1982)

ABSTRACT

The effect of size on ice nucleation has been experimentally investigated for aerosol particles in the aerodynamic range. Aerosol particles are separated according to their aerodynamic diameter while airborne and deposited on a membrane filter which is then developed in a static diffusion chamber. The effect of competition among nuclei and the effect of particle size, though acting together, have been studied separately by sampling various filters in such a way as to obtain a wide range of surface concentrations of particles in each interval of aerodynamic diameter. Moreover, when sampling atmospheric aerosols, the effect of competition among ice nuclei and cloud condensation nuclei is eliminated in practice, as the latter are mostly deposited, together with other small particles, at the end of the filter.

The effect of size has been investigated for homogeneous laboratory dispersed aerosols of clay (montmorillonite, kaolinite and halloysite). Urban aerosols and the exhaust fumes from an oil-fired power station have also been studied.

The usefulness of the technique in investigating the fate of submicron ice nuclei which have become attached to coarser particles has been demonstrated.

1. Introduction

The effect of particle size on the temperature of ice nucleation has been evidenced by many experimental studies. The results of those experiments have been summarized by Rosinski (1979) in three points:

1) For all modes of ice nucleation, each particle size class, even if monodisperse and chemically and physically homogeneous, is always associated with a freezing temperature spectrum.

2) Ice nucleation at a certain given temperature can be initiated by particles of different size.

3) There is, associated with each substance, a certain characteristic temperature of ice nucleation which does not change with a further increase of particle size.

However, the experimental results presently do not permit a relationship between particle size and ice-nucleation efficiency to be precisely determined. It is necessary to establish such a relationship both with regard to homogeneous aerosols and atmospheric aerosols: in the case of homogeneous aerosols, it might provide a new insight into the basic mechanism of ice nucleation, while for atmospheric particles it would help in understanding the history of ice nuclei before their injection into the cloud and to predict their fate within the cloud itself, and hence their

influence on cloud evolution and precipitation development.

When natural ice nuclei are investigated it is particularly difficult to experimentally isolate a size effect, since this may be masked by the fact that aerosol chemical composition also depends on size. Moreover, in nature, larger particles are found in lower concentrations. Georgii and Kleinjung (1967) have found ice nuclei better correlated with larger particles, while Vali (1966) attributes a substantial fraction of them to small particles.

The problem is further complicated by the reasonable suspicion that the effect of size on ice nucleation may be different according to the nuclei's different modes of action: the deposition mode, the freezing mode and the contact mode. Unfortunately, none of the instruments developed up to now for counting ice nuclei are capable of allowing for the three modes of action or can realistically simulate the evolution of temperature and supersaturation in real clouds.

A technique has been developed by Allee *et al.* (1968) to establish a relationship between size and activity of ice nuclei; this consists of capturing particles on collection foils in a Goetz aerosol centrifuge and measuring the activity as in the membrane filter technique. However, the centrifuge does not behave as a real spectrometer, because it uses the whole cross

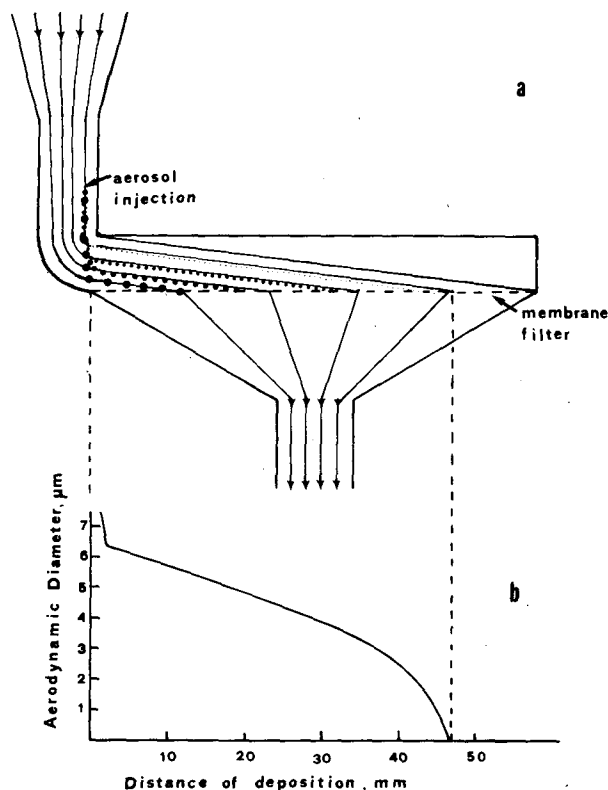


FIG. 1. Scheme of the inertial spectrometer (a) and calibration curve at 0.5 L min^{-1} sampled air and 5.5 L min^{-1} clean air flow rates (b).

section as an aerosol inlet, and it is not readily suitable for field sampling. On the other hand, the spiral centrifuge developed by Stöber and Flachsbart (1969) is a real spectrometer, because the aerosol is admitted through a narrow slit and there is a one-to-one correspondence between particle size and deposition distance, with a very good resolution. Nevertheless this instrument also is not readily suitable for field work and there may be particle losses for sizes exceeding a few micrometers, especially in the high-resolution mode. However both centrifuges have been used in investigating the size dependence of ice nucleating activity, [e.g., during the Third International Workshop on ice nucleus measurements (Gerber, 1976; Cooper, 1976); the fraction of aerosol particles (thermally generated AgI particles) active as deposition ice nuclei was found to be an increasing function of size].

A technique has recently been presented (Prodi, F., *et al.*, 1980) for studying the size dependence of condensation-freezing and deposition nuclei, which combines the aerodynamic particle separation with capture on a membrane filter. This device is portable and can be applied to field aerodynamic spectrometry of natural aerosol particles; the membrane filters are developed for ice nuclei detection in a conditioning

chamber following the extensively used technique first devised by Bigg *et al.* (1963) and improved by Stevenson (1968). In the present work, the size dependence of ice nucleation in homogeneous clay aerosols has been investigated by this technique and measurements have been made of nucleation efficiency of urban aerosols aerodynamically separated on filters.

2. Experimental procedures

Schematically, the spectrometer (Prodi, V., *et al.*, 1979) is composed of a 2 mm deep rectangular channel, with a 90° bend which is flushed with clean air (Fig. 1a). A thin aerosol sheath is injected upstream of the bend. While the streamlines follow the curvature, because of their inertia the particles tend to maintain their initial velocity at the bend and to depart from the original streamline by a distance which is a function of the aerodynamic diameter. The external wall downstream of the bend is made of a membrane filter (Millipore, $0.22 \mu\text{m}$ pore size) through which air flows. The particles are separated while airborne according to their size; the particles' initial slight separation is magnified by the aerodynamic projection against the filter surface. Coarse particles are precipitated at the beginning of the filter; the intermediate sizes, between $10 \mu\text{m}$ and $\sim 0.5 \mu\text{m}$, are continuously separated, and those $< 0.5 \mu\text{m}$, which are too small to be affected, settle at the end of the deposit. A typical calibration curve, obtained in the flow-rate conditions of the majority of the tests (0.5 L min^{-1} of the sampled aerosol and 6.6 L min^{-1} of the carrier gas) is shown in Fig. 1b.

The resolution of the instrument is such that latex sphere particles $> 0.5 \mu\text{m}$ produced by atomizing monodisperse suspensions can be clearly separated in singlets, doublets, triplets and higher multiplicities. The filter can be analyzed for specific applications (microanalysis, scanning for radioactivity, etc.). The small porosity membrane filters we used are well known for the property of capturing particles at the surface, and this is certainly true for particles in the size ranges investigated.

In the present study the filter is developed in a static diffusion chamber similar to that used by Prodi, F., and Wirth (1972). It is well known that chambers flushed with saturated air are more effective in maintaining water saturation on the filters than those based solely on diffusion. To partially reproduce the behavior of the flow chambers some tests were carried out with a small fan gently mixing the air within the chamber. All filters were developed at -18°C , with a surface temperature of the ice corona of -16°C , corresponding to a nominal 20% ice supersaturation and 1.2% water saturation; temperatures have been kept constant within 0.2°C . The growth of the crystals is visually followed with the

naked eye and with a low magnification microscope, and photographs of the filters are taken at selected time intervals. Crystals are counted on equal area strips 1 cm in width, perpendicular to the filter length, each strip corresponding to a range of aerodynamic diameter derived from the calibration curve.

To determine the nucleation efficiency, as a ratio of the number of ice nuclei to that of the aerosol particles on the filter in each size class, the filter is observed with an optical microscope at grazing illumination prior to development, and the aerosol particles are counted. When the submicron particle fraction is of interest a small area of their deposit is cut away and replicated for electron microscopy. In this work we have not taken full advantage of the present aerodynamic separation capabilities of the instrument due to the method followed in counting the ice crystals. This method can be improved and more size intervals can be studied in the small-particle range. Moreover, the separation in this range can actually be increased by changes in the instrument design and by a proper adjustment of the flow rate.

Some aspects of the filter method in ice nucleus measurements must be made clear in advance in order to correctly apply the technique of aerodynamic separation so as to gain information about the dependence on size of ice nucleation.

In the membrane filter method, there is a well known volume effect, wherein ice nuclei concentrations are observed to decrease with increasing sample volume. Lala and Justo (1972) have interpreted this effect to be due to both competition among nuclei and to depletion of the available water vapor by the sampled cloud condensation nuclei (CCN), which in a total sample are uniformly mixed with ice nuclei. The same effects have been considered by King (1978), who has calculated the losses due to hygroscopic nuclei when sampling natural aerosols, in his theoretical work on crystal-crystal vapor depletion. The technique of aerodynamic separation allows the CCN, which belong mostly to the small-particle range, to be deposited at the end of the filter: their influence on other size ranges is therefore practically eliminated. In addition, the competition among ice nuclei and the size effect, though acting together, can be studied under widely different surface concentrations and controlled size ranges so that the two contributions can be evaluated separately.

3. Results and discussion

The first group of experiments was performed with homogeneous, laboratory dispersed clay aerosols—montmorillonite, kaolinite and halloysite. About four filters were sampled for each type of clay in order to cover a wide range of surface concentrations in each size interval.

The results of these tests are shown in Figs. 2–4, where the nucleation efficiency is given as a function of the surface concentration of particles in the different size classes of the clays mentioned. In each indicated size class the nucleation efficiency decreases with increasing surface concentration following a power law, thus indicating that competition among nuclei is a very strong mechanism. It can also be observed that the competition effect is greater for kaolinite and halloysite than for montmorillonite.

However at a specific surface concentration of particles on the filters an effect of size is also apparent. In the range we have investigated, this effect is more evident for montmorillonite and kaolinite than for halloysite. For the first and second kinds of clays the size effect at a given surface concentration of particles has been derived from the experimental curves and is shown in Figs. 5 and 6. When examining these curves it must be borne in mind that the first size class has no upper size limit and the last one has no lower limit. Thus, except for these two intervals, the reference size has been taken at the center of each interval to derive the curves.

Tests with internal mixing of the chamber air have produced higher counts of crystals at equal surface concentrations of particles. The results are shown in Fig. 3 for kaolinite; note that both competition and size effects are also maintained in these conditions.

Since the effects of size and competition always act together, even under different controlled conditions, the possibility that they can be mutually dependent must be considered. We think that the observed size effect is not competition dependent because:

- 1) The competition effect (or volume effect) is determined by ice crystals actually growing on the filter (water vapor sinks) rather than by particle concentration itself.

- 2) If it were competition-dependent it would be observed equally well in all investigated particles. Instead halloysite did show a negligible effect of size even at high surface concentrations of particles. It seems more reasonable therefore to attribute the effect of size to the size-dependent concentration of nucleating sites on the particles rather than simply to their geometric size.

Eventually it seems more reasonable that the competition effect be size dependent for the same argument given in 1). As larger particles are better activated due to the size effect, the decrease in maximum humidity accompanying the increased number of sinks decreases the number of activated particles (or increases the competition). This could explain the slightly lower slopes of the lines referring to larger particles in Figs. 2 and 3.

As an additional comment to Figs. 2–4 it must be remarked that a plateau at sufficiently low surface

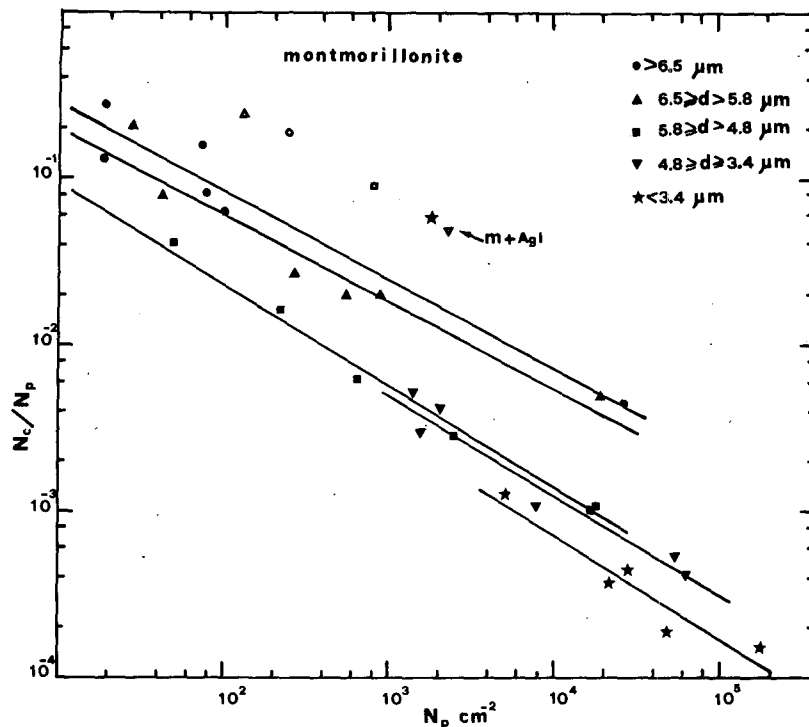


FIG. 2. Nucleation efficiency (the ratio of the number of the crystals to the number of particles) in the indicated size intervals as a function of the surface concentration of particles in the corresponding filter strips for homogeneous aerosols of montmorillonite. Open symbols refer to the test with submicron AgI particles coagulated on coarser montmorillonite particles.

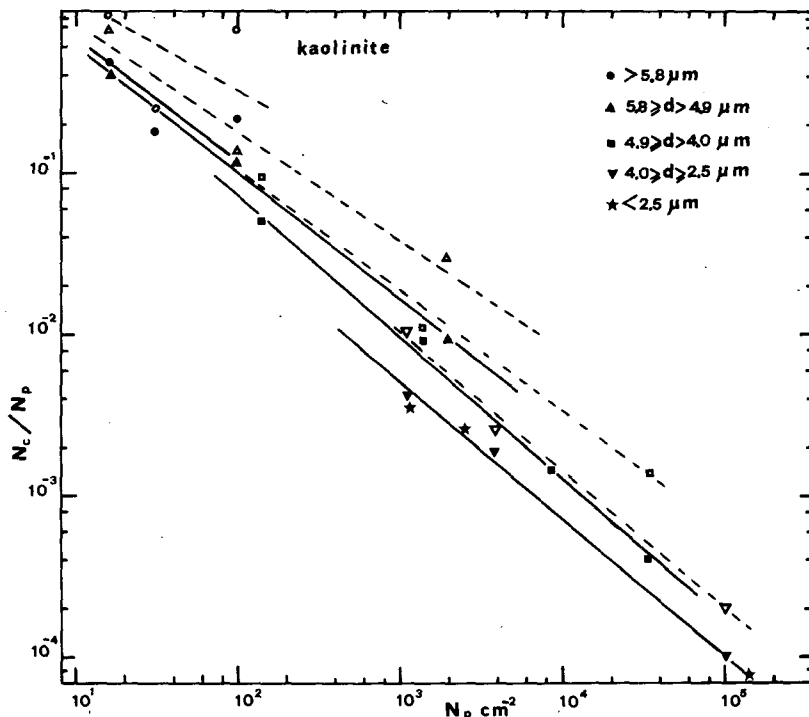


FIG. 3. As in Fig. 2, except for kaolinite particles. Dotted lines and open symbols refer to tests with ventilation inside the chamber.

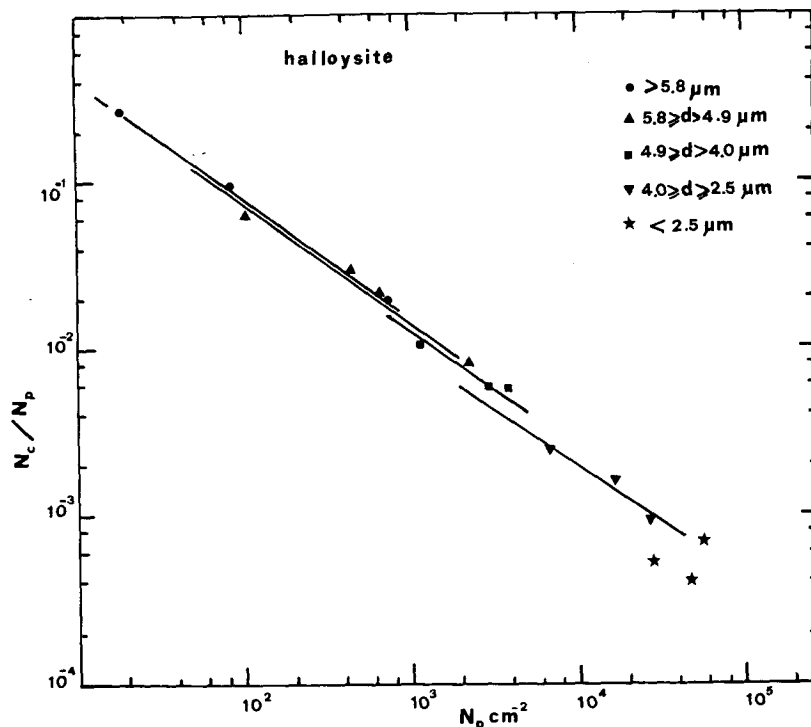


FIG. 4. As in Fig. 2, except for halloysite particles.

concentration of particles should be expected, corresponding to a vanishing competition effect. However the test with ventilation inside the chamber (Fig. 3) demonstrates that the competition among nuclei is also strong at relatively low surface concentrations of particles on filters, while it is not practicable to investigate very low surface concentrations of particles due to the intrinsic background of the technique.

Therefore, we think that the size effect is there in the tested aerosols of clays. In interpreting it we must consider the large gap between nucleation theories and experiments and the possibility that the effect itself is different for the different modes of ice nucleation. First, the explanation of the size effect in terms of Fletcher's theory (1958) must be ruled out as it suggests that the size effect is particularly important only for particles $< 0.1 \mu\text{m}$.

Since the conditions of supersaturation in the chamber during the experiments should have produced nucleation by the condensation-freezing mode, we shall discuss the size effect in this mode, following the treatment of Pruppacher and Klett (1978) and considering the specific surface characteristics of clays. When the particle is immersed in water a large number of water molecules is bonded in small structural units in which some of the molecules are tetrahedrally linked and others have free bonds. If the surface of the solid particles is hydrophobic with

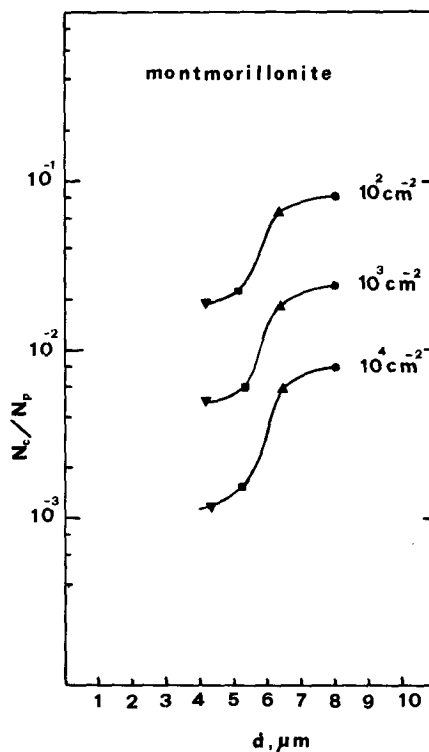


FIG. 5. Nucleation efficiency vs aerodynamic size of particles at the indicated surface concentrations, derived by the experimental lines of Fig. 2, for montmorillonite.

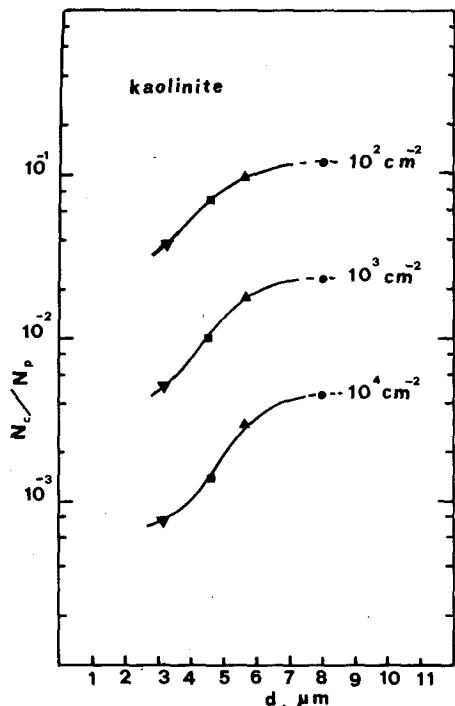


FIG. 6. As in Fig. 5 except for kaolinite.

hydrophilic sites, the molecules with free bonds are preferentially adsorbed on them and fix the structure. If the particle has a uniform affinity for water, water molecules are adsorbed in close packing and more layers are needed for ice to be nucleated. Clay particles have high hydrophilic characteristics but present a surface structure which favors the penetration of water molecules into interstices between adjacent crystallographic layers. In fact all clays have a common structure resulting from the combination of tetrahedral and octahedral units. The various mineralogical components differ in the order of the layers which are held together by weak molecular forces. They also contain many impurities such as carbonates, sulphates and organic substances, due to their sedimentary origin. Water molecules can easily penetrate between nearby layers, be absorbed by the tetrahedron SiO_4 and fix the external hydrated layer. We suggest that the size dependence of ice nucleation that we have observed in the aerodynamic range is due to the proportionality of the points of preferred penetration of water molecules, such as mismatches between the layers, to the surface area of the particles. In montmorillonite, ~80% of the adsorbed water is contained between the expandable layers, which explains its higher plasticity with respect to kaolinite, for which the distance between the expandable layers is constant; halloysite, while structurally similar to kaolinite, has a different arrangement of layers and even a lower water content: hence its size effect is negligible. This interpretation is confirmed by the proved fact that montmorillonite and kaolinite

display a marked preactivation effect (Roberts and Hallett, 1968; Edwards *et al.*, 1970).

An alternative explanation for the effect of size has been suggested by Layton (1973). He has observed that in thin films of silver iodide the interaction between trapped charge and water molecules varies the interfacial free energy, which in turn affects the nucleation characteristics. The size effect, attributed to a change in the ratio of surface states to the total volume as the particle radius decreases, would depend not on the specific geometry of the particle, but on the effect of trapped charges. Though the effect had been demonstrated only for silver iodide, Layton suggested that it might be extended to other substances and that substances may exist for which the size effect would result in an enhancement rather than in a degradation of the ice nucleating ability with the decreasing size. The present experiments, performed on clay particles only, cannot give support to this theory; however, our technique seems promising as a way of testing it, if applied to properly selected substances.

In the case of atmospheric aerosols the size effect also can originate from a possible size-dependent chemical composition of particles. Basically we expect the competition effect to be less evident than for clay particles as in this case only a small fraction of particles are potential ice nuclei at the development temperature. Different surface concentrations of particles in each aerodynamic diameter size class can be obtained by sampling with several instruments at different flow rates, or with one instrument at different sampling periods. If the last procedure is followed the assumption must be made that the sampled aerosols do not change in composition during the sampling period. In any case, since heterogeneous particles are deposited in each size class it must also be assumed that the competition itself is not a more complicated function of the surface concentration.

Urban air has been sampled on filters on two occasions, the first on two subsequent filters and the second on a single filter, and the results are shown in Fig. 7. The best fit line does not have the same meaning here as for homogeneous aerosols because the different effects of competition, size and chemical composition are not separated. In the case labeled ua1 (urban air sampled in Bologna, on 12 June 1981 from 0955 to 1720) there is a weak effect of competition among particles; the last experimental point refers to all particles < 2.5 μm ; since this interval includes a very large number of particles, the nucleation efficiency turns out to be low, in spite of the high surface concentration of crystals in the small-particle region of the filter. In this size interval the number of ice nuclei is probably very much underestimated by both the competition among crystals and the water vapor depletion by condensation nuclei and hygroscopic particles. In the filter labeled ua2 (urban air sampled in Bologna on 17 June 1981, from

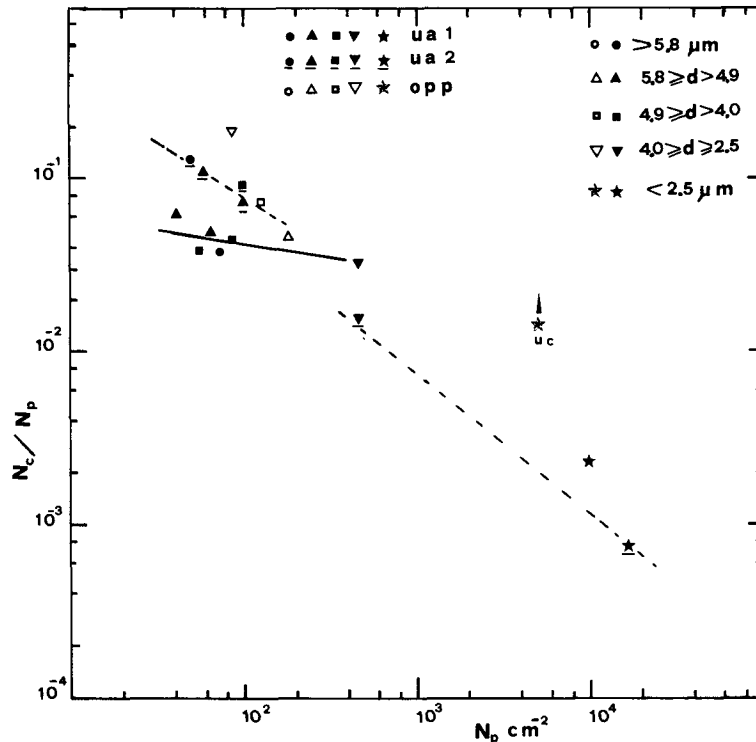


FIG. 7. Nucleation efficiency in the indicated size intervals as a function of the surface concentration of particles for heterogeneous aerosols: ua1, urban air, sampled in Bologna on 12 June 1981; ua2, urban air sampled in Bologna on 17 June 1981; opp, exhaust from oil-fired power station sampled at the stack base. The dotted lines are approximate fits to experimental points suggesting a possible size effect around 4 μ m size.

1050 to 1745) the effect of competition is more evident, and dotted eye-fit lines of experimental points suggest the existence of two populations of particles of different origin and chemical composition. However, when particles in the free atmosphere are investigated a better statistic is needed, with several instruments sampling simultaneously at widely different sampling rates, as previously suggested.

Size could be an important parameter in the case of artificial cloud seeding where particles are produced in the ultrafine range and can evolve rapidly by mutual coagulation or by coagulation on preexisting particles. This situation has been simulated by mixing, in a bag, fan-resuspended montmorillonite particles with hot-wire generated AgI particles. The aerosol was sampled by means of the spectrometer and the filter was developed in the usual way. The filter has shown a much higher nucleation efficiency than montmorillonite alone. The nucleation efficiency is shown in Fig. 3 with open symbols; there is not enough information to separate the competition effect from the size effect. Unattached particles are too small to be separated and are deposited in the fine-particle strip; here the concentration is too high for the crystals to be counted individually. This feature also appeared on a filter which sampled the ex-

haust of an oil-fired plant at the stack base. In this case the existence of two separate populations of ice nuclei was evidenced not only by the different filter regions affected but also by the different onset time of the crystals. Within ~ 8 min of development only crystals in the range 4–7 μ m of particles were observed; then after an additional 7 min countless crystals appeared in the fine-particle strip. The nucleation efficiency concerning this test is also reported in Fig. 7.

The onset time of the first crystal is a very reproducible parameter during the filter development. This time ranged from less than 1 min in the filters which sampled urban air to 2 min for kaolinite, 6 for halloysite, 8 for montmorillonite, and 4 for montmorillonite with AgI particles attached.

The region of the filter where the first crystals appear is an effect of both size and surface concentration of particles for homogeneous aerosols. Most frequently, in our tests, crystals appear first in the intermediate-size interval regions of the filter and then spread toward the regions of smaller and coarser particles. When testing urban air filters quite different situations are encountered. Sometimes it has been observed that crystals appear in the large-particle side and then spread in fronts of equal size contours.

On other occasions it was observed that the first crystals appeared in large numbers in the small-particle size range of the filter. However, as mentioned above, it has not been possible in these tests to separate the role of size and that of possible differences in chemical composition accompanying the variation in size.

4. Conclusions

It has been demonstrated that the aerodynamic separation of aerosol particles on a filter support is auxiliary to studies of basic aspects of ice nucleation by condensation-freezing and deposition, as it allows an experimental validation of the mechanisms proposed for the effect of size of homogeneous aerosols of different substances.

The effect of size on ice nucleation has been studied for homogeneous particles of various clays, in the size range where aerodynamic separation is effective. The same study has been shown to be possible for heterogeneous particles of atmospheric origin, while their chemical composition can also be investigated in its size dependence. If the effect of competition among nuclei is determined, the technique directly provides the concentration of ice nuclei in each class of aerodynamic diameter in the sampled air, with no need to know the corresponding aerosol concentration. This information is very important in studies of cloud evolution, cloud modeling and weather modification.

In the examined samples most of the ice nuclei have been found in the $>1 \mu\text{m}$ range: however the technique immediately shows when ice nuclei in the range $<0.5 \mu\text{m}$ are present. In such cases sampling with the inertial spectrometer can be complemented with sampling through diffusion devices; these yield information on the diffusion coefficient and hence on the behavior of fine and ultrafine particles. A correction for penetration into the diffusion stages of large particles can be made with the size information gained with the spectrometer in the aerodynamic range.

A better understanding of some aspects of the filter technique can be gained as a byproduct of the aerodynamic separation, by depositing in each filter region almost monodisperse particles in the required surface concentrations. The competition of condensation nuclei for the available water vapor is almost eliminated as they are mostly deposited at the end of the deposit. It is suggested that for a correct interpretation of ice nuclei measurements obtained with the membrane filter technique not only the temperature and supersaturation must be specified, but also the surface concentration of the sampled particles on the filter. Conversely, the discrepancies among measurements of ice nuclei reported by different authors could be reduced if a reference surface concentration of particles were taken for the measurements.

Further applications of aerodynamic separation

are shown to be possible, such as the study of ice nuclei attached to coarser particles, with effects on artificial and inadvertent weather modification, or a systematic investigation of the size of ice nuclei in air masses of different origin.

Modifications to the design of the instrument and to the airflow are under way, in order to expand the separation in the small-particle range.

Acknowledgments. The research has been sponsored by the Piano Finalizzato "Promozione della qualità dell'ambiente," CNR.

REFERENCES

- Allee, P., H. Gerber and H. K. Weickmann, 1968: Determination of the sizes of ice nuclei with an aerosol spectrometer. *J. Rech. Atmos.*, **1-2**, 167.
- Bigg, E. K., S. C. Mossop, R. T. Mead and N. S. C. Thorndike, 1963: The measurement of ice nucleus concentrations by means of Millipore filters. *J. Appl. Meteor.*, **2**, 266-269.
- Cooper, W. A., 1976: Ice nucleus measurements using a Stöber centrifuge. *The Third International Workshop on Ice Nucleus Measurements*, Gabor Vali, Ed., University of Wyoming, 63-74.
- Edwards, G. R., L. F. Evans and A. F. Zipper, 1970: Two-dimensional phase changes in water adsorbed on ice-nucleating substrates. *Trans. Faraday Soc.*, **66**, 220-234.
- Fletcher, N. H., 1958: Size effect in heterogeneous nucleation. *J. Chem. Phys.*, **29**, 572-576.
- Georgii, H. W., and Kleinjung, 1967: Relations between the chemical composition of atmospheric aerosol particles and the concentration of natural ice nuclei. *J. Rech. Atmos.*, **3**, 145-156.
- Gerber, H., 1976: Activity and size of aggregate thermal AgI particles. *The Third International Workshop on Ice Nucleus Measurements*, Gabor Vali, Ed., University of Wyoming, Laramie, 75-90.
- King, W. D., 1978: Vapor depletion in processing membrane filters: The effects of chamber parameters. *J. Appl. Meteor.*, **17**, 1498-1509.
- Lala, G. G., and J. E. Jiusto, 1972: Numerical estimates of humidity in a membrane filter ice nucleus chamber. *J. Appl. Meteor.*, **11**, 674-683.
- Layton, R. G., 1973: Ice nucleation by silver iodide: a new size effect. *J. Colloid Interface Sci.*, **45**, 215-216.
- Prodi, F., G. Santachiara, V. Prodi and T. De Zaiacomo, 1980: An experimental technique to study the effect of size on ice nucleation. *J. Appl. Meteor.*, **19**, 1448-1450.
- , and E. Wirth, 1972: Ferromagnetic particles and ice nuclei. *Tellus*, **34**, 568-573.
- Prodi, V., C. Melandri, G. Tarroni, T. De Zaiacomo, M. Formignani and D. Hochrainer, 1979: An inertial spectrometer for aerosol particles. *J. Aerosol Sci.*, **101**, 411-419.
- Pruppacher, H. R., and J. D. Klett, 1978: *Microphysics of Clouds and Precipitation*. D. Reidel 714 pp.
- Roberts, P., and J. Hallett, 1968: A laboratory study of the ice nucleating ability of some mineral particulates. *Quart. J. Roy. Meteor. Soc.*, **94**, 25-34.
- Rosinski, J., 1979: The role of natural and man-made ice-forming nuclei in the atmosphere. *Advances in Colloid and Interface Science*, Vol. 10, Elsevier, 315-367.
- Stevenson, C. M., 1968: An improved Millipore filter technique for measuring the concentration of freezing nuclei in the atmosphere. *Quart. J. Roy. Meteor. Soc.*, **94**, 35-43.
- Stöber, W., and H. Flachsbarth, 1969: Size-separating precipitation of aerosols in a spinning spiral duct. *Environ. Sci. Tech.*, **3**, 1280-1296.
- Vali, G., 1966: Sizes of atmospheric ice nuclei. *Nature*, **212**, 384-385.