An Investigation of the Size-Supersaturation Relationship of Soluble Condensation Nuclei

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ABSTRACT

The activation supersaturation of several artifically prepared NaCl aerosols was measured in the laboratory using a thermal gradient diffusion chamber. Size distributions of these aerosols and total particulate concentrations were determined with a Whitby Aerosol Analyzer and a Gardner Small Particle Detector. From a combination of these data, the relationship was derived between supersaturation and necessary minimum size of the particles for nucleation. This experimentally obtained correlation indicates that, at a given supersaturation, a NaCl particle has to be two to three times larger than theory predicts in order to be active as a cloud condensation nucleus. Possible explanations for the discrepancy are discussed.

1. Introduction

The general theory of heterogeneous condensation of water vapor as reviewed, for instance, by Fletcher (1962), basically correlates size and some physicochemical properties of the nucleating particles with water vapor supersaturation. Especially in the case of soluble hygroscopic nuclei, such as NaCl, the theory is quite straightforward and provides a relationship of nucleus size versus critical supersaturation which has found general acceptance and is widely used in cloud modeling. Recently, Junge and McLaren (1971) presented calculations extending that relationship for nuclei composed of a mixture of soluble and insoluble material.

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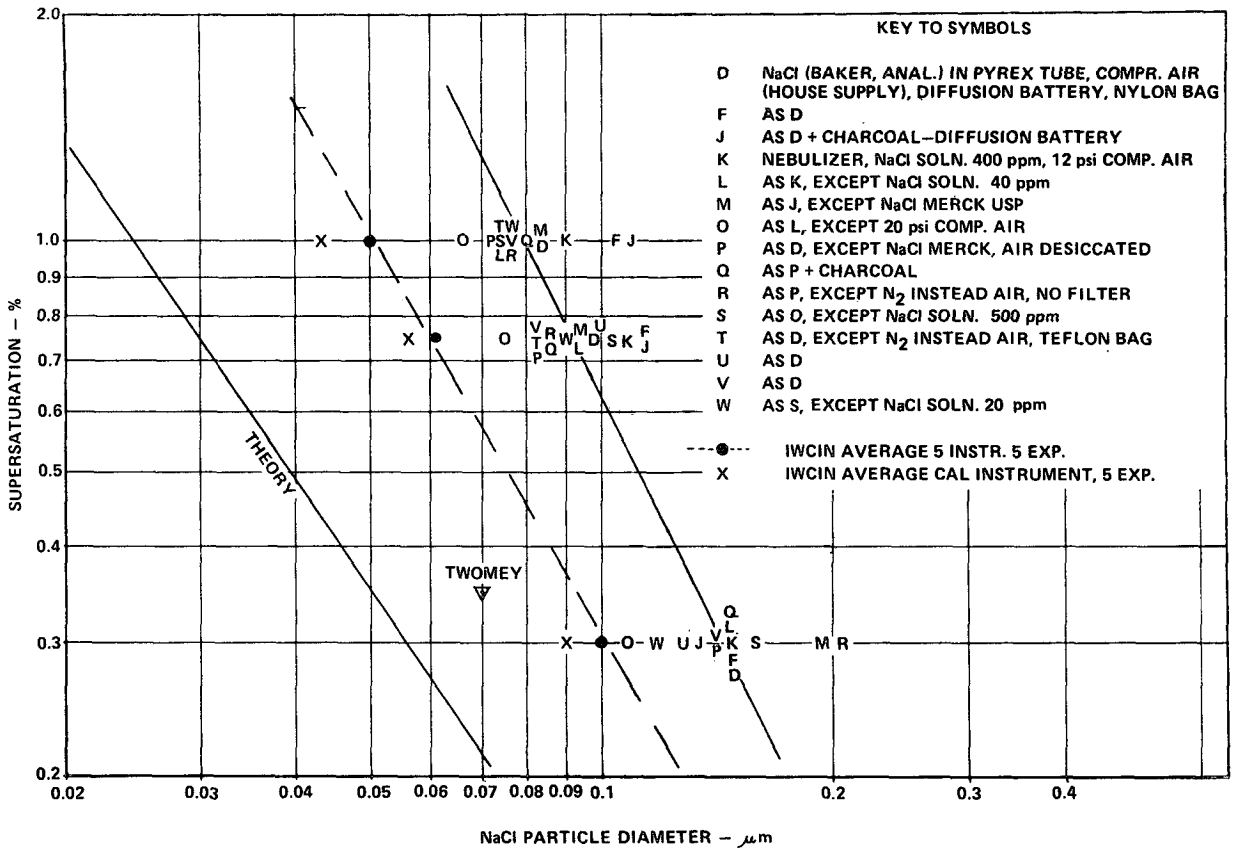

FIG. 1. Critical supersaturation vs apparent NaCl particle diameter (dry).

Experimental investigations of this theory are scarce, mainly because of lack of suitable instrumentation to measure particle sizes in the difficult range around 0.1 μm. Twomey and Severynse (1964) and Twomey (1965) reported experiments where natural aerosol sizes were estimated by diffusion battery methods and related to critical supersaturations. Due to the unknown composition of the aerosol, their results are difficult to interpret except that supersaturations were considerably higher than theory predicted for, say, NaCl; this, however, is not surprising since the nuclei sampled were of a mixed nature and therefore not likely to be quite as effective as condensation nuclei of pure NaCl. The one explicit value given by Twomey in which particle size is related to critical supersaturation is entered in Fig. 1.

During the Second International Workshop on Condensation and Ice Nuclei (IWCIN) held in Ft. Collins, Colo., August 1970, experiments were performed in which comparisons of the various cloud condensation nuclei counters were made using artificial NaCl aerosols. Since the complete particle size spectra of the NaCl aerosols were established by the Minnesota Aerosol Analyzing System (MAAS) (Whitby and Husar, 1971a), a unique opportunity arose for comparing the theoretical size-supersaturation values with experimental findings.

The averaged results of five experiments with five different cloud chambers as presented by Ruskin and Kocmond (1971) are shown as a dashed line in Fig. 1. The solid line to the left side of the figure represents the theoretical values (as tabulated in Mason, 1957). The IWCIN data indicate that a NaCl particle must be about twice as large as calculated in order to reach the critical size at a given supersaturation. Although the five instruments did not agree as well in the case of artificial nuclei as they did for natural particles, there can be no doubt that they all, in combination with the MAAS, showed a definite trend toward larger than predicted critical size.

Because of the small number of NaCl experiments and the emphasis on instrument intercomparison, no attempt was made to pursue the problem during the IWCIN. Although a number of possible reasons for the phenomenon come to mind (which will be discussed later), it was felt that, prior to attempting an explanation, more evidence had to be gathered.

With the cooperation of the staff of the University of Minnesota Particle Technology Laboratory, the authors conducted another series of experiments involving the Cornell Aeronautical Laboratory (CAL) thermal diffusion chamber (Kocmond and Mack, 1972) and the MAAS.

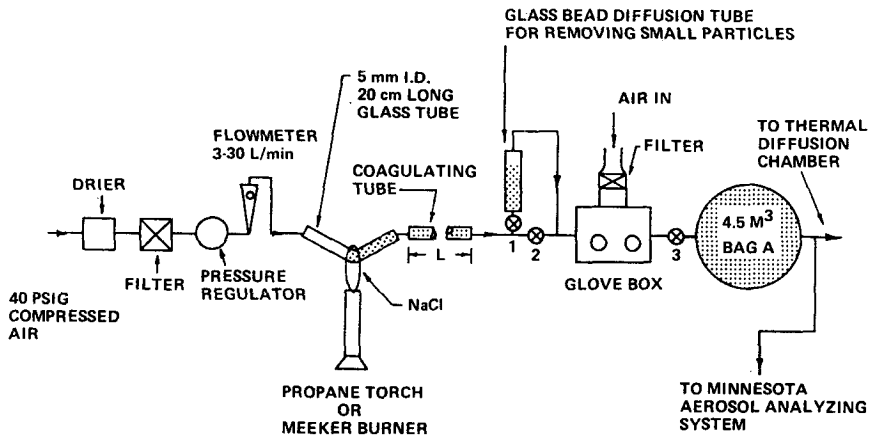

FIG. 2. Schematic of NaCl aerosol generator (Whitby and Husar, 1971b).

2. Experimental setup

The experimental arrangement employed at the University of Minnesota was simpler and more compact than that used at the IWCIN, although most of the components were the same. In order to link the experiment with those of the IWCIN, NaCl was again chosen as the nucleating substance and small particle generation was identical with the IWCIN procedure (Whitby and Husar, 1971b) as depicted in Fig. 2. Alternately, a second method of particle generation was used whereby a medical type pneumatic nebulizer containing a dilute NaCl solution was placed in the glove box where final particle dilution takes place. A 4.5 m^3 nylon bag or a 1.5 m^3 Teflon bag served as aerosol storage containers. One to two meter latex tubes (1.0 cm i.d.) were secured to the bag outlets in order to transfer nuclei to the various instruments. Two units of the Whitby Aerosol Analyzer (WAA), the most important component of the MAAS in the size range of interest, were used to provide additional comparisons.

In order to clarify the results of the IWCIN, it was intended to first duplicate the workshop experiments and then vary a number of parameters which were considered potentially influential in altering the NaCl aerosol during its generation.

The experimental procedure consisted of first analyzing the size and concentration of the aerosol in the storage bag. As this was being done, part of the air sample was gently forced into the thermal diffusion chamber and allowed to come to rest. Active NaCl nuclei in the test sample grow to droplet sizes within a few seconds and can be photographed before falling out. Nucleus concentration is determined from the number of droplet images counted on the close-up photographs taken at 90° to an intense, narrow light beam passing through the chamber. The supersaturation within the diffusion chamber was calculated from measured temperatures of the moist top and (colder) bottom surfaces of the chamber. The critical size of a NaCl nucleus at a given supersaturation (i.e., the particle size for which droplet growth will proceed without limit) was determined by finding that particle size on a cumulative size distribution which corresponds to the nucleus concentration measured in the diffusion chamber.

3. Experimental results and discussion

Some 20 runs were performed, and the results of most experiments are plotted in Fig. 1. (A few tests were terminated prematurely because of difficulties in obtaining the proper concentration of particles.) Also shown are the average CAL data from NaCl experiments performed at the IWCIN (as crosses). The pertinent procedural variations in the NaCl aerosol generation during the University of Minnesota tests are shown in the legend of Fig. 1.

Two different sources of NaCl were used (Baker anal., Merck USP) mainly to assure that no accidental contamination could have influenced the entire series of measurements. Another potential source of contamination was thought to be in the air which was passed over the evaporating NaCl. Therefore, the compressed air was filtered and desiccated and occasionally purified over charcoal; an alternative was to use purified nitrogen from bottles. In some cases, the diffusion battery was by-passed to eliminate any additional contaminants. In order to avoid any detrimental effects which might arise from heating the salt in the pyrex tube, several runs were carried out with aerosols from evaporated mists of NaCl solutions of various strengths. Occasionally, a Teflon bag was used instead of the nylon storage bag in order to eliminate any influence of a particular contaminant related to this part of the equipment. Fig. 1 clearly indicates that, on the average, the required minimum size for activation of NaCl particles is three times the theoretically predicted value (at least for supersaturations ranging from 0.3 to 1%). Furthermore, the above-mentioned variations of the experimental conditions did not change the outcome of

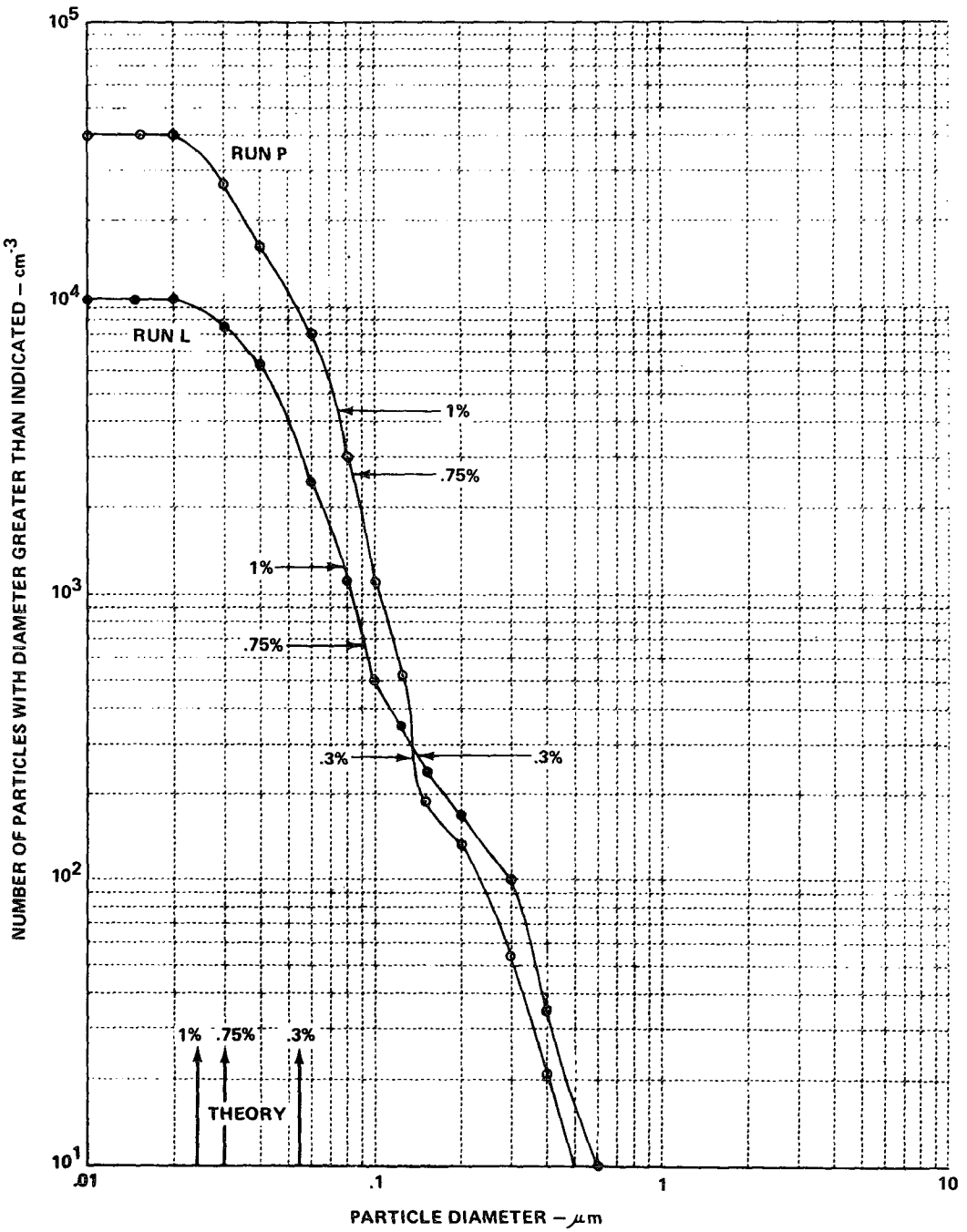

FIG. 3. Typical cumulative size distribution of NaCl aerosols.

the experiments in any consistent manner; the scatter of the data points is within the expected range considering the various steps involved in determining size and supersaturation. However, the fact that these measurements—carried out with particular care—show an even greater difference from theory than the IWCIN results is quite surprising.

It seems extremely improbable that more than a small part of the discrepancy between theory and experiment could be attributed to systematic errors in the instrumentation. From the examples of two typical runs shown in Fig. 3 (horizontal arrows indicate observed concentrations of activated nuclei; vertical arrows show the theoretically predicted values), it is evident that the WAA would have to measure all particles too large by a factor of 3 or their number too high by nearly an order of magnitude in order to account for the differences between experiment and

theory. However, for the particle size range in question, the WAA is certainly better than 20% in accuracy (Whitby and Husar, 1971a), and recent electron microscopic calibration by Tomaides[2] points to even smaller errors, compensation for which would rather increase our discrepancy.

On the other hand, if certain shortcomings of the thermal diffusion chamber were responsible for the deviation from theory, it would mean, as Figs. 1 and 3 show, that only about 10% of the potentially active nuclei were recorded or that the supersaturations were only one-fifth as great as calculated from temperature difference measurements. In a recent review of diffusion chamber design, Squires (1971) discussed various features which could lead to erroneous results. The only critical point applying to our case is the somewhat excessive particle concentration used in some of the experiments. At 1% supersaturation, for example, approximately 10^3 nuclei cm^{-3} are considered the upper limit above which the measured nucleus concentration is smaller than the actual number of nuclei present. Our values ranged from 1×10^3 to 5×10^3 nuclei cm^{-3} at 1% supersaturation. This effect may have influenced the present experiments toward finding too large particle diameters; however, the experimental data did *not* show a systematic variation with changes in nucleus concentration. This suggests that no major error was introduced by working with relatively high nuclei concentrations (which were necessary for proper operation of the WAA).

The above considerations combined with the fact that several trial runs were performed to eliminate possible sources of error related to equipment, carrier gas, etc., lead us to suspect the presence of impurities adsorbing on the surfaces of the freshly formed nuclei. This surface contamination would modify the particle's activity as a condensation nucleus, thus requiring a higher activation supersaturation than theory predicts for an ideal NaCl particle. In this context, it is worthwhile citing recent experiments by Knight (1971) in which water vapor condensing on reasonably pure NaCl crystal surfaces was found to form distinct droplets rather than covering the whole surface uniformly. This unexpected phenomenon may have been a manifestation of the same factors which influenced the findings reported here. Since efforts to examine NaCl particle behavior in a "pure" nitrogen atmosphere did not reveal any significant differences in the activation spectra, it is possible that trace contaminants in the NaCl could have produced the suspected adsorbed monolayer on the nuclei studied. At this stage of the investigation, however, no details of such an activity-reducing process can be proposed.

A weakness in the theory would seem an obvious alternate explanation for the discrepancies observed; however, it is very difficult to find deficiencies in the model other than neglect of possible surface effects of the kind just mentioned above.

[2] Personal communication.

4. Alternate experimental approach

An experiment currently in progress aims to resolve the problem of determining the relationship of nucleus size and critical supersaturation by using a more direct method of particle size measurement. The basic idea is to sample the droplets formed inside the diffusion chamber immediately after they have grown on the nuclei that are introduced into the chamber. Upon evaporation from the sampling surface, the residue can be considered the material which constitutes the condensation nucleus and, in special cases, the mass of the nucleus can be determined. Since removal of the droplets from the chamber for the purpose of sampling would disturb the moisture regime, capture of the droplets has to take place inside the chamber. In practice, this is accomplished by propelling a 3-mm electron microscope sample substrate (copper grid with formvar layer) at high speed through the diffusion chamber. With a chamber diameter of 7 cm, the swept-out volume is approximately 0.5 cm^3. In order to guide its motion, the sample grid is attached to the circular end of a 3-mm diameter metal rod which is projected through the chamber. The velocity presently used is 45 m sec^{-1}, providing a reasonable collection efficiency of about 70% or better for droplets >7 μm diameter. This was determined from a photographic droplet record taken just prior to the shot, combined with droplet replicas obtained by replacing the sample grid with a drop sensitive coat (Eosin B).

NaCl particles generated by evaporating a fine mist of dilute salt solution serve as a test aerosol since NaCl crystallizes into easily recognizable shapes from a pure solution droplet impinging on a formvar substrate. This has been demonstrated by applying the described capture method (outside of the diffusion chamber) to the NaCl solution mist prior to its desiccation.

Due to insufficient collection efficiencies for droplets $\lesssim 7$ μm diameter, actual samples in the chamber are, so far, taken only at supersaturations of 2–3% where droplets grow large enough to be sampled. Preliminary results of the electron microscopic examination indicate that much fewer distinct NaCl crystals are present than expected and, for the most part, ill-defined flat objects appear. Although one could speculate that contaminants prevented the NaCl from crystallizing in its usual compact form, thus supporting a previously mentioned contamination hypothesis, this needs to be investigated further, especially by extending the sampling capability to smaller size droplets (i.e., lower supersaturations).

5. Conclusions

Although this study does not offer an explanation for the deviation from theory found in these and the

IWCIN experiments, it strongly suggests that calculations and conclusions obtained by applying the theoretical values of particle nucleating efficiency have to be viewed with great caution. This can be illustrated, for instance, by considering that Junge and McLaren's (1971) critical supersaturation-dry radius curve for a particle composed of 5% soluble and 95% insoluble material coincides with the present experimental values obtained for carefully prepared pure NaCl. Additional experiments should be performed using other techniques of particle sizing and nucleus detection in order to help resolve this apparent discrepancy between theory and experiment.

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