

AN INVESTIGATION OF THE MELANDER EFFECT

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ABSTRACT

Melandar's experimental results on the apparent production of salt nuclei by evaporation of salt solutions are examined both theoretically and experimentally. It is concluded theoretically that the rate of evaporative escape of molecular sodium chloride or other salts from sea water is too low by a factor of 10^{18} to account for the formation of the nuclei active in cloud condensation. It is shown experimentally that the rate of collection of salt particles of diameter in excess of 0.05 micron over evaporating salt solution is too low by a factor of at least 10^6 to account for the observed rate of atmospheric condensation. Therefore, there appears to be no basis for accepting Wright's suggestion that Melander's work provides an answer to Simpson's long-standing objection to the sea-salt hypothesis of condensation nuclei.

1. Introduction

In an interesting series of papers published a number of years ago, Wright (1939; 1940a; 1940b) and Simpson (1939) debated the question of the nature and origin of atmospheric condensation nuclei. Simpson rejected Wright's hypothesis that the nuclei are chiefly sea-salt particles and did so on the basis of two principal considerations: first, the shapes of Wright's visibility-humidity curves were continuous through that particular relative humidity (about 78 per cent) at which Simpson felt that crystallization should have rapidly extinguished the light-scattering power of any brine droplets present; second, a computation of the average rate of production of spray droplets required to account for the rate of cloud condensation for the earth as a whole gave Simpson a rate of spray-drop formation so large (order of 10^4 cm⁻² sec⁻¹ over stormy seas) as to appear quite implausible.

It has been pointed out by Mason and Ludlam (1951) that the work of Dessens appears to remove Simpson's first objection by revealing that brine droplets of nuclear dimensions do not crystallize at the concentrations representing saturation of bulk solutions in contact with undissolved solute, but rather remain liquid down to relative humidities as low as 50 per cent for drops initially 1 to 10 μ in radius. Mason and Ludlam suggest that the rate of either homogeneous nucleation or heterogeneous nucleation within so tiny a system is probably so small as to preclude phase transition until considerable salt saturation is attained (homogeneous nucleation) or until chance encounter with a suitable foreign particle occurs (heterogeneous nucleation),

each of which possibilities must be expected to permit a brine droplet to persist in liquid form for some time after salt saturation is attained under conditions of slowly falling relative humidity.

On the other hand, Wright sought to meet Simpson's second main objection to the sea-salt hypothesis by invoking the work of Melander (1897). Melander reported that slides exposed to warm but not boiling salt solutions developed "salt stains," which he attributed to salt particles that might have escaped from the solution in the course of the evaporation of the solution. Wright admitted that the details of the process needed further attention, but observed that Melander's hypothesis had never been refuted. The present writers have long regarded this hypothesis as very improbable, so we have sought to investigate both theoretically and experimentally the likelihood that Wright might be correct in suggesting that the Melander effect could provide the answer to Simpson's second objection. The theoretical results, though they follow from arguments that are correct only to order of magnitude, render inadmissible any simple evaporative hypothesis. The experimental results agree in showing that only minute amounts of salt in the form of particles large enough to serve as condensation nuclei can be collected over evaporating salt solutions, and that even these minute amounts can be almost completely accounted for in terms of the traces of salt normally present in the atmosphere.

2. Theoretical considerations

Neither Melander nor Wright clearly specified a physical process by which salt might leave the ocean surfaces in spray-free regions, but their implications (which have gone unchallenged so long) seem to point most directly to some type of evaporative escape. In this section, it will be shown quantitatively that

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evaporation of molecules of NaCl from salt solutions proceeds at so slow a rate as to be utterly incapable of providing support for Wright's position. It will also be pointed out qualitatively that there are very good reasons for doubting still more seriously the importance of escape of any NaCl aggregates larger than single molecules.

In any solution for which the vapor tension of one component (as H_2O in a salt solution) is known to be less than that for the same component in the pure state, it is necessarily true that the vapor tension of the second component (as salt in an aqueous salt solution) is also reduced below the value for the pure form of that second component at the same temperature. This follows from the fact that each such vapor-tension reduction is due to the effects of intermolecular attraction between the two species comprising the solution, implying a mutual lowering of the rate of escape into the vapor phase. If, then, one estimates the vapor tension of the second component (salt) in its pure form, he has at most an *upper* limit on the vapor tension of that component after solution has occurred.

This estimate can readily be made for the simple case where NaCl is the only salt in solution, and this will give a sufficient indication of how the more complex mixture of sea salts must behave. From tabulated values of the latent heat of vaporization and of the latent heat of fusion of NaCl at its melting point, the heat of sublimation of crystalline NaCl is found to be about 880 cal/g near the melting point. Neglecting, conservatively, the normal increase of heat of sublimation with decreasing temperature, one may use this value of the heat of sublimation along with the measured value of the vapor tension of NaCl at its melting point [5×10^3 dyne/cm² (Lange, 1939)] to compute the vapor tension of crystalline NaCl at, say, 300K, by use of the Clapeyron equation. The computed vapor tension, 10^{-24} dynes/cm², is at most an upper limiting value to the vapor tension of NaCl when present in an aqueous solution, as has been pointed out above, so it may be used here without unfair prejudice toward Melander's hypothesis and Wright's argument.

Next one may estimate q , the mass rate of bombardment of NaCl molecules per unit area of surface exposed to fully saturated NaCl vapor of 10^{-24} dynes/cm² pressure. This rate is given by

$$q = p/(2\pi RT)^{1/2} \approx 10^{-28} \text{ g cm}^{-2} \text{ sec}^{-1},$$

where p is the saturation vapor-pressure of NaCl, and R is the gas constant per gram of NaCl vapor. If one assumes, conservatively, a condensation coefficient of unity here, this value also represents an upper limit to the mass *efflux* of NaCl molecules from a solution, a conclusion that follows from the usual equilibrium

arguments applied to evaporation-condensation balance.

Now to meet Simpson's second objection by an appeal to the Melander effect, one would have to demonstrate that it accounts for a steady salt efflux of some 10^{-10} g cm⁻² sec⁻¹. Hence the above calculation, though only approximate, shows that Wright's position is untenable; for the rate of evaporative escape of NaCl molecules from a smooth sea, though not zero, is too low by a factor of the order of 10^{18} to satisfy the demands of Simpson's objection.

To add still further indication of the improbability of Wright's suggestion, one may calculate the density of the NaCl vapor in equilibrium with a sea surface, and from that density deduce the NaCl-NaCl collision rate in the sea air. Even fully NaCl-saturated vapor is found to contain only about one NaCl molecule in 10^4 m³, and the associated collision rate is of the order of 10^{-15} cm⁻³ sec⁻¹. Coagulation of NaCl molecules into aggregates large enough to serve as atmospheric condensation nuclei would thus be intolerably slow, even without taking account of the further and exceedingly serious difficulty posed by the usual free-energy barrier to spontaneous growth of aggregates by molecular collisions.

Over and above the essentially thermodynamic objections raised above, a fundamental obstacle to the escape of NaCl (or other sea salts) is implied in the fact that the physical chemist has established fairly conclusively that, when ionic salts enter into aqueous solution, the anion and cation are for the most part separately solvated by the polar water molecules. The Na^+ ion is believed to have a hydration number of 8 to 10, while that for Cl^- is 4 to 5 (Levy, 1953); so either an appreciable number (12 to 15) of water molecules must be imagined to leave the solution along with each NaCl molecule, or else an uncomfortably large number of hydration bonds must be simultaneously broken, and this just prior to a particularly favorable collision that activates the residual (Na^+ , Cl^-) pair for evaporative escape from the solution.² The first possibility, escape of a sort of polymer of a dozen or so water molecules in attendance upon an (Na^+ , Cl^-) ion-pair, is rendered extremely improbable by virtue of the inherent difficulty of imparting kinetic energy to a large mass (solvated complex) by means of bombardment with particles of small mass (individual H_2O molecules), added to which is the unfavorably high probability that each incident molecule will spend its kinetic energy in merely dissociating the very loosely coupled hydration complex with which it collides. The second possibility,

² Levy's hydration numbers are computed from considerations of electrolyte viscosity and may be higher than the equilibrium number of solvent molecules that are tightly bound at any one time; but the effect of hydration is still large, even if one halves his values.

desolvation followed by acquisition of escape energy, can be seen to demand so much nicer a concatenation of favorable events as to warrant even less consideration.

It may be noted that, from Wright's (1940b) comments on the Melander effect, one almost seems justified in drawing the conclusion that he envisaged the salt as leaving the solution in the form of tiny droplets carried out by evaporating water molecules. If by "minute droplets" Wright meant any aggregates larger than one solvation complex of the type just discussed above, the thermodynamic and kinetic probability of the alleged process must fall to an infinitesimal value.

Thus, an attempt to form a theoretical estimate of the rate of evaporative escape of single salt molecules, as well as an effort to consider qualitatively the mechanism of escape of aggregates of water and salt molecules, seem to force one to the conclusion that the Melander effect can scarcely be of meteorological importance and that Simpson's famous second objection has surely not been met by Wright. There remains, to be sure, a logical need to repeat Melander's original experiments under more carefully controlled conditions, with special attention given to evaluating the effects of possible contamination by externally airborne salt particles. Results of an experimental study of just this type will now be described.

3. Experimental test of the Melander effect

The discovery of analytical techniques involving *Millipore*³ as a collection medium (Lodge, 1953) makes possible the detection of very small particles. By this means, individual particles of sodium chloride down to at least 0.5- μ dry diameter may readily be distinguished by characteristic spot reactions. Still smaller particles, down to about 0.05- μ dry diameter, are retained quantitatively and, if numerous, reveal themselves by forming a distinct cirriform deposit on the filter. Hence, an experimental check of the Melander effect can now be made with use of a technique of previously unattainable sensitivity. If salt particles or solution droplets large enough to serve as condensation nuclei do escape from quietly evaporating salt solutions, this new analysis technique should detect them.

The apparatus consisted of a vertical glass tube or column, 2.5 m high and 8.5 cm in diameter. The bottom was closed by a rubber stopper carrying two glass tubes: a short one connected to a leveling bulb for the introduction of brine, and a longer one, bent over at the top, by means of which a current of air could be directed down onto the surface of the solution. The top of the column was fitted with a two-

hole stopper. A rubber hose attached to an aerosol-type Millipore holder fitted snugly through the larger hole in this stopper, so that the holder hung a short distance inside the tower, and all air which entered through the air inlet had to leave through the Millipore. The other hole carried a static pressure line to the leveling bulb, so that pressure changes inside the column would not affect the liquid level. The entering air passed through a rotameter and a filter of U. S. Chemical Corps type-6 filter paper.

In operation, 3 per-cent sodium chloride solution was admitted to the bottom of the column until the surface level was about 10 cm below the air-inlet nozzle. At this height no visible splashing of the solution occurred, although the surface was deformed by the impinging jet of air. The intake air was adjusted to six liters per minute, and the Millipore was put into sampling position, some 2 m above the surface. The air-flow rate used was sufficient to give linear ascent rates up the tower of about 2 cm/sec, which should have supported all particles smaller than about 2- μ diameter.

The apparatus operated continuously for *seven days*. The liquid level was readjusted daily to compensate for evaporation; however, some dried material did deposit on the walls, and this could account for the production of a few salt particles as will be discussed below.

By the end of seven days, 400 cm³ of water had been evaporated. The Millipore was removed, floated on a slightly acid 5 per-cent solution of mercurous fluosilicate for 5 min, washed twice by agitation in distilled water, dried, placed on a microscope slide covered with immersion oil, and examined for the characteristic reaction areas (Lodge, 1953). From the size of these areas, the size of the original particles could be calculated (Lodge and Fanzoi, to be published). The entire surface of the filter showed only thirty such areas, corresponding to dry sodium-chloride particles of 5.3- μ mass-mean diameter.

Next a blank was run under conditions identical to those just described, except that all salt solution was removed from the column and the entire apparatus

TABLE 1. Number distribution of collected sodium-chloride particles by size class.

Equivalent dry diameter (μ)	Number of particles in test run	Number of particles in blank run
0-1	0	2
1-2	2	2
2-3	6	4
3-4	3	4
4-5	8	6
5-6	9	2
6-7	1	4
7-8	1	0
Total	30	24

³ *Millipore* is the trade name of a membrane filter manufactured by the Lovell Chemical Company, Watertown, Mass.

carefully washed with distilled water and dried before start of the run. In this blank run of seven days, a total of 24 particles of mass-mean diameter $5.0\ \mu$ (dry size) were detected. Results of both the test and the blank are shown in table 1.

That the blank run gave so many particles may seem surprising, and in fact no completely satisfactory explanation can here be given for this result. The filtered air passing through the collection system in each of the two runs probably contributed only a few particles to each total. An estimate of this contribution, based on filter characteristics, total airflow, and previous rough estimates of atmospheric salt-particle concentrations, gave a figure of two or three such particles; but this estimate can only be regarded as correct to order of magnitude. Once salt particles have been introduced into a system, it is found to be extremely difficult, if not impossible, to remove them completely; so some contamination of the blank run must have occurred from the filter holder, from the walls of the column, and from the initial air charge of the column. As will be pointed out later, this very persistence may have been the cause of Melander's erroneous conclusions.

Application of the t test to the difference between the mean particle diameters found in the two runs gave the result that the difference was not significant ($t = 1.1$ for $29 + 23 = 52$ degrees of freedom, implying about 25 per cent probability that as large a difference might result simply from errors of random sampling from a single homogeneous population of particle sizes). A single test run and a single blank do not permit any conclusions to be drawn as to the statistical significance of the difference between the *total numbers* of particles found in the two cases. However, in view of the extended period of time (seven days) over which each run was made, we feel that the similarity of the two results provides rather strong evidence that a Melander effect played no part in the production of the few salt particles found in the test run. The unavoidable crystallization of small amounts of salt on the walls of the column just above the slightly fluctuating meniscus, followed by chance detachment, may be invoked to explain the small residual difference. It should be emphasized that particles too small to be detected by this technique, if any existed, could have little meteorological significance. In fact, Junge (1953) has shown fairly conclusively that virtually no sodium chloride is found in the natural atmosphere in the form of particles smaller than about $0.8\text{-}\mu$ diameter. Hence, any important contribution of the Melander effect to the salt economy of the atmosphere should have been detected by this experiment if the effect were real.

It is to be noted that the residual difference between

the test and blank runs is a number of orders of magnitude larger than the theoretical estimate of purely evaporative escape made above. We do not believe that this must be taken as contradicting that estimate, since a single adventitious particle of a few microns dry size would yield a measured rate enormously larger than the predicted evaporation rate. In any event, collisional aggregation of evaporated molecules into particles of the order of a few microns in diameter seems entirely out of question under the conditions of this experiment.

The experimental results can be used to obtain one further argument, a very strong one, against the importance of Melander's hypothesis. Let us for the moment assume very conservatively that *all* of the particles found in the test run were due to Melander's postulated process. Then thirty particles, having a mass-mean diameter of about $5\ \mu$, were produced by the evaporation of $400\ \text{cm}^3$ of salt solution. The mean rate of evaporation of the ocean surfaces, estimated from the global mean precipitation rate, is of the order of $0.2\ \text{cm/day}$. Hence, each square centimeter of ocean surface would give, at the experimentally observed rate, one particle every seventy days, approximately. Simpson (1939) has calculated that, to account for the mean rate of cloud condensation over the earth, the entire ocean surface would have to produce an average of about $10^3\ \text{particles cm}^{-2}\ \text{sec}^{-1}$, all of which must escape and become active condensation nuclei. This required value exceeds our measured rate by some nine orders of magnitude. Converting to units of mass, which are somewhat more favorable to Wright's argument, since Simpson's assumed particles were far smaller than those found in this experiment, one finds that the measured rate of salt transfer to the air, approximately $10^{-17}\ \text{g cm}^{-2}\ \text{sec}^{-1}$, is still about a million-fold too small. Thus, aside from all considerations of the reality of the difference between test and blank, the measured *total* rate of salt production in the test run fails by an extremely large factor to account for the production of natural condensation nuclei.

Melander's original results still remain to be explained. In the light of current knowledge, salt particles could have been picked up on his slides in the following ways:

1. Airborne salts present could have been carried to the slides, since it appears from Melander's description of his work that incomplete precautions were taken to exclude outside air, which normally contains traces of salt;
2. In several cases, Melander's solutions had previously been boiled; the cloud of salt particles carried into the air by active boiling is extremely persistent, and could easily have contributed to the observed results;
3. In other cases, the brine was warmed; although no active boiling had taken place, dissolved gas would come out of the solution in bubbles, which might carry considerable salt into the airspace he sampled in his covered containers.

4. Summary

The following conclusions have been reached here:

1. The rate of evaporation of salt from a solution is, according to thermodynamic considerations, too low by a factor of perhaps 10^{18} to account for the production of condensation nuclei; aside from this enormous deficiency in the simple mass-efflux rate, there is a further serious difficulty in the extremely small rate of collisional aggregation of salt molecules at the equilibrium densities predicted theoretically;

2. Considerations of the physical chemistry of salt solutions render it even less likely that evaporative processes could lead to the escape of salt in the form of particles larger than one molecule; hence, Wright's suggestion that "particles of salt" may be carried out of solution by evaporating water molecules cannot be regarded seriously;

3. An experimental determination of the rate of collection of salt particles of diameter greater than 0.05μ over a quietly evaporated solution revealed no significant difference between a test run and a blank run;

4. Even if *all* of the salt collected in a seven-day test run were produced by the hypothetical Melander effect, it would imply an oceanic salt-production rate that is too low by a factor of about 10^6 on the basis of a mass-flux calculation, and too low by a factor of about 10^9 on the basis of a particle-flux calculation, to support Wright's position;

5. Melander's original results can very probably be explained by one or more types of contamination which he took no apparent precautions to avoid;

6. Simpson's long-standing objection to the sea-salt hypothesis of cloud condensation cannot, therefore, be regarded as having been removed by Wright's appeal to Melander's hypothesis.

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