Comments on "Anomalous Deliquescence of Sea Spray Aerosols"

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1. Introduction

Pueschel *et al.* (1969) discuss the variation of light scattering due to natural and artificial sea spray aerosols as a function of relative humidity. Their data indicate a stronger growth with humidity of an artificial sea salt aerosol (3% by weight NaCl, 0.2% MgCl₂, 0.1% MgSO₄) and of a NaCl aerosol than has been previously observed for natural sea spray aerosols or

spray aerosols produced from natural sea water. They suggest that this difference is due to the anomalous solubility of natural sea water caused by the presence of dissolved organic matter.

2. New experimental studies

We have recently completed a detailed study of aerosol growth with humidity which has not yet been

FIG. 1. Weight increase (or relative mass) of hygroscopic aerosols as a function of relative humidity. The various growth curves are defined as follows:

- No. 1. Theoretical curve of NaCl (after Robinson and Stokes, 1955).
- No. 2. Curve of natural sea salt (Kientzler and Arons, 1952), where m_0 is the mass of dry, water-free salt.
- No. 3. Average curve of natural sea salt containing water of crystallization. The data points indicate increasing (●) and decreasing (◐) relative humidity.
- No. 4. Average curve of giant maritime aerosol particles ($r > 0.8 \mu$) from Helgoland, 26–28 September 1966. The data points indicate increasing (Δ) and decreasing (▽) relative humidity.

The crosses (x) for increasing and + for decreasing relative humidity are the data points for artificial mixture 1, while the circles (○) for increasing and ◐ for decreasing relative humidity refer to mixture 2 (see text). The cross-hatched curve is that of curve 2 corrected for 12–14% water of crystallization; the horizontally hatched area is the recrystallization area of supersaturated solutions.

published. This study provided data which may be of interest for this discussion. Impactor samples of aerosols or the residues of evaporated solutions are exposed to air of variable relative humidity and their variation in water content is measured by a microbalance (Winkler, 1969). Some measurements relevant to the present problem are presented in Fig. 1 in which the weight increase of aerosol samples is plotted against the relative humidity. The weight increase is defined as m_w/m_0 , where m_w is the mass of water absorbed by the aerosol sample at relative humidities (r.h.) $> 20\%$ and m_0 the weight of the aerosol sample at r.h. $< 1\%$, i.e., the dry aerosol mass. All measurements were performed at a temperature of 25°C. Curve 1 was calculated for pure NaCl from data by Robinson and Stokes (1955) above 75% r.h., the humidity of the saturated solution. Test runs with our method showed excellent agreement with these data. Curve 2 was calculated for sea salt according to the vapor pressure measurements of Kientzler and Arons (1952). Their data, given in chlorinity Cl , were converted into salinity S (‰) by applying the equation, $S = 1.811Cl + 0.07$. The difference between these two curves is due to the fact that for the same relative humidity salt mixtures show higher concentrations than solutions of pure salts (see, e.g., Braitsch, 1962, p. 108). We also studied five different sea salt samples, using sea water from the Atlantic (near the African coast, at 25°30'N, 15°W, 10 m deep) and the Baltic (four samples at 19°15'E, 54°36'N at the surface and 25 m deep and at 19°50'E, 57°03'N at the surface and 230 m deep). While composition of water from the Baltic is almost the same as in the other oceans (Table 1), the salinity is lower, but this is of no importance for the present study. We chose the Baltic samples because of their greater probability of containing dissolved organic matter. We measured these salt samples—as is usually done—with first increasing, then decreasing, humidity.

3. Discussion

We will first discuss the data for increasing humidity. For all five samples the cluster of values (dots) show very little difference so that the dashed average curve can be regarded as fairly representative for natural sea water. At 33% r.h. the growth starts because $MgCl_2$ goes into solution. The $MgCl_2$ solution then dissolves fractions of other salts. The growth continues until at about 75% r.h. the bulk of the NaCl goes into solution. Above 75% our m_w/m_0 data points lie below those of curve 2 because, after drying, natural sea salt contains water of crystallization (crystal water) whereas curve 2 was calculated assuming no crystal water. Heating 22 of our sea salt samples to 300°C gave an average crystal water content of 14.3% by weight. In oceanographic techniques sea salt is usually heated to 600°C for direct salinity determinations (Harris and Riley, 1964) and no decomposition occurs. Since we heated only to 300°C the

loss in weight must be due to crystal water alone. If we correct the data of Kientzler and Arons for a crystal water content of 12–14% (always referred to water-free salt), we obtain the hatched area, the left border of which refers to 14%, in good agreement to our measured value and with curve 3.

The ratio m_w/m_0 is very sensitive to the presence of crystal water because it affects both the denominator and the numerator in opposite ways. Curves 2 and 3 differ at 85% r.h. by a factor of 1.25, and curves 1 and 3 by a factor of 1.35 (this factor is not constant with humidity).

As a general rule we found for all aerosol and salt samples that the m_w/m_0 values for decreasing humidity were larger than for those of increasing humidity if the solutions were supersaturated. In Fig. 1 this is shown for curve 3 by the dots with a vertical bar. This hysteresis is due to incomplete nucleation of the solid phase and depends on various factors such as the cleanliness of the sample or the influence of the collection surface, and is usually not reproducible. Since we cannot exclude the influence of the collection surface in our method, airborne particles can be expected to show higher and more reproducible supersaturations. In our measurements the hysteresis effect can be eliminated only by completely drying the sample to less than 1% r.h.

In addition to natural sea salt we studied two artificial salt mixtures prepared from analytically pure salts. Mixture no. 1 was composed of 78.3% NaCl, 9.6% $MgCl_2$, 5.7% $MgSO_4$, 3.6% $CaSO_4$, 2.6% KCl and 0.25% $CaCO_3$ (all values refer to crystal water free substances) and was prepared according to Riley and Skirrow (1965). The observed growth curve for increasing (crosses) and decreasing (plus signs) humidity is in good agreement with that of natural sea water. Mixture no. 2 was prepared in accordance with Pueschel *et al.* and consisted of 91% NaCl, 6% $MgCl_2$ and 3% $MgSO_4$. For this mixture, increasing humidity (open circles) gave smaller values below 75% and larger values

TABLE 1. Ionic composition of sea salt and artificial mixtures (percent by weight).

Ion	Sea salt		Artificial mixtures	
	Atlantic ^a	Baltic ^b	No. 1 (This measurement)	No. 2 (After Pueschel <i>et al.</i> , 1969)
Na	30.7	30.7	30.8	36.0
Cl	55.1	55.1	55.8	59.4
SO ₄	7.73	7.8	7.3	2.4
Mg	3.7	3.76	3.6	2.1
Ca	1.18	1.19	1.16	—
K	1.1	1.1	1.27	—
CO ₃	0.4		0.15	
Others	0.2			
	100.1	99.65	100.11	99.9

^a From Riley and Skirrow (1965).

^b From Kremling (1969).

TABLE 2. Values of m_w/m_0 and extinction coefficient ratios at r.h. = 80% for various natural and artificial salts.

Parameter	Salts			
	NaCl	Sea salt without crystal water	Artificial mixture 2	Average for natural sea salt
m_w/m_0	3.35	3.10	2.85	2.50
m_w/m_0 (normalized to sea salt)	1.34	1.24	1.14	1.00
Extinction coefficient ratio				
$p=2$	1.21	1.16	1.09	1.00
$p=3$	1.34	1.24	1.14	1.00

above 75% as compared to natural sea water. This is due to the fact that this mixture corresponds to an ionic composition which is somewhat different from natural sea water composition as indicated in Table 1. The composition of sea salts from the Atlantic, the Baltic and artificial mixture 1 are in close agreement, whereas that of mixture 2 differs considerably. The crystal water of mixture 2 was calculated as 9.2%, as compared to a measured value of 8.8%. These differences in the crystal water content and composition are responsible for the differences of the growth curves shown in Fig. 1. However, the spread is still much smaller than that to be expected from the optical measurements of Pueschel *et al.*

Fig. 1 also shows the data from three samples of giant maritime aerosol particles ($>0.8 \mu$ radius) collected over the period 26–28 September 1966 on the island of Helgoland. Over the ocean surface particles of this size consist almost completely of pure sea salt (Woodcock, 1953; Moore and Mason, 1954) if the trajectories of the air masses exclude any influence by continents. This was the case for our samples. The individual data are plotted as triangles with the dotted line representing the average. Below 75% the giant particles grow a little faster, above 75% a little slower than pure sea salt. The hysteresis effect is similar to the other cases.

Crystallization of all the sea salt occurs in the horizontally hatched area. The scatter within this area depends on numerous factors as mentioned above; the present method does not allow one to obtain reproducible data on this hysteresis effect but it can be expected that airborne aerosol particles would show better agreement with the right-hand limit of this area, i.e., show maximum hysteresis.

4. Analysis and conclusions

We will now try to interpret the light scattering data by Pueschel *et al.* on the basis of the data in Fig. 1.

Comparison of our growth curves with Fig. 1 of Pueschel *et al.* indicates that the data on light scattering must correspond to the branch of increasing humidity in agreement with Pueschel's information that his scat-

tering data were obtained for a stepwise increasing humidity. However, since Pueschel *et al.* dried the air only down to 30–40%, it is likely that the hysteresis effect was not completely eliminated and that the difference in hysteresis between the various salts is partly responsible for the differences in light scattering. From our Fig. 1 we can draw the following conclusions:

1) Our data indicate good agreement for total water uptake between 20 and 90% r.h. for the following cases: (i) calculated growths from the vapor pressure measurements by Kientzler and Arons (1952) if 14% crystal water (as found in sea water) is taken into consideration; (ii) measured growth curves of artificial sea salt (mixture 1) and five samples of natural sea salt; and (iii) measured growth curves of natural sea salt aerosol samples collected over the North Sea under conditions which made it certain that the particles consisted almost completely of sea salt (the slightly lower growth is most likely due to the influence by maritime aerosol components other than sea salt). This agreement demonstrates conclusively that the vapor pressure behavior of sea salt including that of natural sea spray particles is controlled predominantly by the ionic composition. The role of dissolved organic material, if present at all, is negligible and cannot explain the discrepancies found by Pueschel *et al.*

We have tried to extract, from evaporated aliquots of sea water samples collected close to the sea surface, any organic material which might have been dissolved. Within weighing accuracy ($\lesssim 0.5\%$) no difference was found.

2) NaCl (not shown in Fig. 1) and the artificial sea salt (mixture 2) used by Pueschel *et al.* show practically no growth at 40% relative humidity (the lowest humidity used by these authors) in contrast to the actual sea salt samples. This difference is due partly to a larger hysteresis and partly to a larger fraction of constituents like magnesium salts which have already dissolved at humidities above 30%. For sea salt the ratio m_w/m_0 at 40% r.h. is ~ 0.1 – 0.15 , as indicated by the two arrows in the lower right-hand corner of Fig. 1. This mass ratio corresponds to a radius ratio of

$$\frac{r}{r_0} = \left(\frac{m_w \rho_0}{m_0 \rho_w} + 1 \right)^{\frac{1}{3}} \approx 1.07\text{--}1.11,$$

where ρ_0 is the density of sea salt (2.2 gm cm^{-3}) and ρ_w the density of water (1.0 gm cm^{-3}). The corresponding ratio of the extinction coefficients would be $(r/r_0)^p$, with $2 < p < 3$, or in our case ~ 1.14 – 1.37 .

At 80% r.h. the ratio determined by Pueschel *et al.* (their Fig. 1) is ~ 1.3 – 1.4 and it is clear that hysteresis at 40% r.h. and/or slightly higher hygroscopicity of sea salt will contribute to this effect but are not sufficient to explain its magnitude.

3) The influence of crystal water is the most important factor as shown in Table 2.

The ratio of the extinction coefficients in this case is more than sufficient to explain the effect found between sea water and the artificial sea salt mixtures used by Pueschel *et al.* One would expect, however, to find differences from these data between pure NaCl and mixture 2 which the authors do not find. If both the hysteresis effect and that due to crystal water are involved, the product will influence the resulting growth difference to an extent sufficient to explain the differences in light scattering of a NaCl and a sea spray aerosol.

It should be taken into consideration, however, that the data of Pueschel *et al.* show considerable scatter and also that the light scattering curves may be influenced by optical effects. For instance, it is possible that the scattering characteristics of dry salt particles are different from those of droplets because they are neither spherical nor homogeneous. This is particularly true for dry NaCl particles which even at 40% r.h. have a coating of a concentrated solution of magnesium salt. Similar to effects known from melting snow flakes (Kerker *et al.*, 1951), a thin coating with liquid may modify the scattering characteristics of salt crystals.

Summarizing, we conclude that the optical effects found by Pueschel *et al.* do not require the assumption of the influence of organic matter but can be explained on the basis of normal physico-chemical behavior of salt solutions.

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