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Adsorption of Water on 8−15 nm NaCl and $(NH_4)_2SO_4$ Aerosols Measured Using an Ultrafine Tandem Differential Mobility Analyzer

Sami Romakkaniemi,[†] Kaarle Hämeri,[‡] Minna Väkevä,[§] and Ari Laaksonen*,[†]

Department of Applied Physics, University of Kuopio, P.O. Box 1627, 70211 Kuopio, Finland, Finnish Institute of Occupational Health, Topeliuksenkatu 41 a A, 00250 Helsinki, Finland, and Department of Physics, P.O. Box 9, 00014 University of Helsinki, Finland

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Adsorption of water on aerosol particles has been measured using an ultrafine tandem differential mobility analyzer. The measurements were made with NaCl and $(NH_4)_2SO_4$ particles, between 8 and 15 nm in mobility diameter, at room temperature. The adsorption was found to be stronger on larger particles, indicating that the Kelvin effect plays a significant role in adsorption on ultrafine particles. Different adsorption isotherms were fit to the data and calculated for planar surface using the fitted isotherm constants. The measurements indicate that more than one layer of water molecules is adsorbed on both substances below the deliquescence relative humidity. Adsorption on NaCl was found to be stronger than on $(NH_4)_2SO_4$.

Introduction

A thin film of water molecules coats many substances under ambient conditions. Salt particles form aqueous solution droplets at the deliquescence relative humidity (DRH) specific to the material and temperature. The DRH for NaCl, for example, is 75.3% at 298 K.[1] Adsorption occurs at relative humidities below DRH, and a recent study by Peters and Ewing[2] suggested that water adsorbed on NaCl(100) surface is in the liquid phase. A water layer on aerosols may affect the scattering and absorbance of radiation and thereby have a direct influence to the radiation balance of the Earth. Water films formed on aerosol particles may also have important consequences for heterogeneous chemistry in the atmosphere as the kinetics of many heterogeneous reactions are strongly dependent on the phase of aerosol particles (see e.g. Knipping et al.[3] and references therein). These reasons give strong motivation for measuring the amount of adsorbed water on sodium chloride and ammonium sulfate aerosols.

The adsorption of water on NaCl is a widely investigated topic, both experimentally[2,4] and through computer modeling.[5,6] In these studies the main attention has been paid to the NaCl(100) surface. Adsorption on other salts, like ammonium sulfate, has not been studied as intensively or not at all. In the atmosphere, NaCl is important in marine areas, but elsewhere ammonium sulfate is usually present at higher concentrations. The available studies on $(NH_4)_2SO_4-H_2O$ interactions are mainly focused on the deliquescence behavior of ammonium sulfate aerosols (see e.g. Cziczo and Abbatt[7] and references therein).

The most frequently applied techniques in experimental adsorption studies are microscopy and infrared spectroscopy. In this study, we apply an instrument which has previously not been used in adsorption studies, the tandem differential mobility analyzer (TDMA). Since 1978[8] the TDMA has been used to determine the hygroscopic properties of aerosols, and nowadays it is a standard method in determining the hygroscopic growth of submicron particles at a given relative humidity. The amount of water adsorbed on such particles below the DRH is very small, and therefore, the measurement technique has to be very sensitive to the particle size changes. The relative size change due to adsorption is of course larger the smaller the particles are, which makes it possible to detect adsorption on nanometer-sized particles. In this paper we present measurements of adsorption of water on 8−15 nm NaCl and $(NH_4)_2SO_4$ aerosols carried out using the recently developed ultrafine tandem differential mobility analyzer (UF-TDMA) technique.[9]

The data examined in this paper are subsets of data presented in two earlier works.[9,10] The experiments were designed for measurement of the hygroscopic growth of nanometer-sized particles, and it was somewhat surprising for us to realize that water adsorption on the particles at relative humidities below DRH can be seen in the data. Unfortunately, the apparatus used for the experiments is no longer at our disposal, and we therefore have to settle for analysis of the existing datasets, which do not have complete RH coverages and which show some scatter that could probably have been avoided had the experiments been specifically designed for adsorption measurements. Nevertheless, we believe that the datasets offer valuable information for atmospheric scientists and demonstrate the usefulness of the TDMA instrument in adsorption studies.

Experimental Section

The ultrafine tandem differential mobility analyzer that was used in this work has been fully described elsewhere.[9] This technique is based on the use of two differential mobility analyzers (DMA) in series together with an aerosol conditioner. The TDMA teqhnique has earlier been successfully used in studies on hygroscopic growth of individual aerosol particles. In principle, any process leading to changes in size can be investigated (e.g. evaporation, condensation, adsorption, or liquid phase chemical reactions). However, there are requirements to be met which limit the number of practical applications.

A brief description of the apparatus and experimental procedure is presented herewith. The primary components of

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* Corresponding author.

[†] University of Kuopio.

[‡] Finnish Institute of Occupational Health.

[§] University of Helsinki.

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the UF-TDMA include DMA1, the aerosol flow RH conditioner, DMA2, the DMA2 sheath air RH conditioner, and the particle counter. The measurements presented in this paper were carried out using laboratory-generated ammonium sulfate and sodium chloride aerosols. The aerosol was produced using a standard method of atomizing a solution of distilled and deionized milli-Q water containing 0.1% by mass $(NH_4)_2SO_4$ or NaCl. The atomization was done using a commercial particle generator (Atomizer, TSI model 3076). The resulting aerosol was diluted and dried below the crystallization humidity of the solution droplets (RH $<$ 10%) by mixing with dry filtered air at room temperature.

DMA1 is used to select particles of known size from the polydisperse input aerosol. Before entering the DMA1, the particles were charged to an equilibrium using a radioactive source. The humidity of the flow after DMA1 containing monodisperse aerosol is adjusted to a selected value in the aerosol conditioner. In this study, this value was typically kept 3% lower than the humidity of the sheath air of DMA2. The final RH results from mixing of aerosol air and sheath air inside the DMA2. The ratio of aerosol flow to sheath air flow was 1:10, and RH inside the DMA2 was thus rather close to that of the sheath air of DMA2. The resulting particle size was measured with DMA2, and the particles were detected with a condensation particle counter (TSI 3010).

The basic requirement in using a TDMA technique is that the experimental conditions leading to size changes are well controlled. One of the crucial features is that any (unwanted) change in size after the aerosol conditioner (e.g. inside DMA2) has to be eliminated. This requirement is fulfilled as the humidity and temperature of the surrounding air are actively controlled and remain practically unaltered after the RH conditioner and inside DMA2.

The sensitivity of the experimental technique depends on the relative change in size which has to be large enough. A significant diameter growth factor is traditionally taken to be 1.02 or larger. Therefore, the investigations related to adsorption on the surface have to be performed with small enough particles so that already one monolayer causes a significant relative size change. The UF-TDMA setup is specially designed for studies of particles in the size range of ca. 10 nm, which is well applicable for quantitative adsorption studies. However, it has to be noted that the measurements presented in this paper were a part of an investigation concerning the hygroscopic growth of particles, where the growth of particle diameter is much larger than growth due to adsorption. Therefore, the experimental setup was not fully optimized for adsorption studies. This is probably seen in the scatter of the experimental data shown in the following.

Theory

The growth factor (GF) resulting from the UF-TDMA experiments is the particle diameter change as a function of relative humidity. It is defined as

$$\mathrm{GF} = \frac{d_{\mathrm{RH}}}{d_{\mathrm{dry}}} \qquad (1)$$

where d_{dry} is the diameter of the dry particle and d_{RH} is particle diameter at the prevailing RH.

(a) Size of Nonspherical Particles. Electron microscopy carried out in our previous work[10] indicates that the dry NaCl particles are almost cubic. The nonspherical shape affects the mobility diameter of the particles, and we therefore have to correct for the nominal NaCl diameters (8, 10, and 15 nm). With large particles, the volume equivalent diameter is obtained by dividing the mobility equivalent diameter by a shape factor χ, which for cubic particles has the value 1.08.[11] Particles in the 10 nm size range have diameters smaller than the mean free path of air molecules, reducing the resistance of air to the motion of the particles. The reduction can be described with a Cunningham slip correction factor[11] $C(d)$. Several equations have been presented for $C(d)$ in the literature;[12] we adopt the following experimental formula for solid particles:

$$C(d) = 1 + (133/d)[1.142 + 0.588\exp(-0.999d/133)] \qquad (2)$$

The volume equivalent diameter d_{V} can now be obtained from the mobility equivalent diameter d_{m} of nonspherical transition regime particles using[13]

$$d_{\mathrm{V}} = \chi^{-1}\frac{C(d_{\mathrm{V}})}{C(d_{\mathrm{m}})}d_{\mathrm{m}} \qquad (3)$$

In our case, the mobility equivalent diameter d_{m} equals the dry diameter d_{dry} obtained from the DMA data. After the shape correction is applied, the resulting values for the volume equivalent dry NaCl diameters are 7.70, 9.62, and 14.42 nm.

In our previous papers[9,10] we compared the measured hygroscopic growth with growth curves based on the hygroscopicity experiments of Tang and co-workers.[14,15] They used the electrodynamic balance technique which measures changes of particle mass rather than volume, and their results are therefore not affected by particle shape. Our data for NaCl were in much better accord with the results of Tang et al.[15] when the shape correction was made, which is one of our strongest reasons for applying the correction here. However, for ammonium sulfate particles the agreement between our results[9] and those of Tang and Munkelwicz[14] was reasonable without any shape correction. This is consistent with the general perception that ammonium sulfate particles are much more spherelike than sodium chloride. We therefore do not make a shape correction for $(NH_4)_2SO_4$ particles.

As water is adsorbed on NaCl particles, their shape is likely to become more and more spherical. However, we are considering particles with a maximum of two monolayers of water on them, and it is probable that they remain more cubic than spherical in shape. (Accounting properly for the rounding of the particles would require a molecular dynamics study, which is beyond the scope of this paper.) We thus obtain the volume equivalent diameter of the particles with adsorbed water on them simply by multiplying the volume equivalent dry NaCl diameters by the experimental growth factor.

(b) Adsorption Isotherms. The amount of adsorption is generally expressed in terms of surface coverage Θ (number of monolayers adsorbed). This quantity can be obtained from the growth factor provided the monolayer thickness is known. We take the monolayer thickness to be 1.9 Å, which corresponds to the number obtained by Stöckelmann and Hentschke[5] in a molecular dynamics study of water adsorption on NaCl. Engkvist and Stone[6] found a similar thickness for the first monolayer on NaCl using the Monte Carlo technique; however, the second and third layers were found to be somewhat thicker. Because we have no information concerning the monolayer thickness on ammonium sulfate, we apply the same number as for sodium chloride.

The amount of adsorbed matter is usually described by adsorption isotherms. One of the best known and simplest equations is the Langmuir isotherm which presents the coverage Θ as

$$\Theta = \frac{bp}{1 + bp} \tag{4}$$

where p is the partial pressure of the gas being adsorbed and b is constant specific to the surface material and temperature. The basic assumption behind the Langmuir isotherm is that adsorption is unimolecular so it cannot be used when more than one layer is adsorbed.

One of the most frequently used equations for multilayer adsorption is the BET (Brunauer, Emmett, and Teller) isotherm. It is based on the idea that each separate layer obeys the Langmuir equation and the average heat of adsorption is equal to the heat of condensation for the second and higher layers. The BET isotherm is given by

$$\Theta = \frac{cS}{(1 - S)(1 - S + cS)} \tag{5}$$

where S is the gas saturation ratio and c is a constant. This theory assumes that the number of layers goes to infinity as the saturation ratio approaches unity.

Another isotherm for multilayer adsorption is the so-called FHH (Frenkel, Halsey, and Hill) isotherm defined as

$$\ln\left(\frac{1}{S}\right) = \frac{A}{\Theta^B} \tag{6}$$

where A and B are constants. This isotherm is based on potential theory. It assumes that a potential field at the surface of a solid decreases with a power of distance that can be treated as adjustable parameter.

(c) Kelvin Effect. Adsorption layers are stable because of attractive interactions between adsorbate molecules and the underlying material, which reduce the chemical potential of the adsorbed phase with respect to bulk liquid. However, the chemical potential is further modified if the surface is highly curved. For example, it is well known that adsorption layers are thicker on the walls of small pores than on flat surfaces of the same material at given vapor saturation ratio. Similarly, it has been experimentally confirmed that the surface coverage is lower on surfaces of nanometer-sized particles compared with flat surfaces.[16] The curvature effect can be accounted for using the Kelvin equation (see e.g. Zhu et al.[17] and references therein). A Kelvin correction term for the equilibrium vapor pressure of an adsorbed phase on a spherical particle can be written as

$$C_K = \exp\left(\frac{2\sigma v_w}{RT(r + t)}\right) \tag{7}$$

where σ is the gas−liquid surface tension of the H_2O−adsorption layer, v_w is the molar volume of adsorbed water, R is the gas constant, T is temperature, r is the diameter of the aerosol particle, and t is the thickness of the adsorption layer.

We stress that in eq 7 the molar volume and the surface tension differ from the bulk liquid values. The molar volume v_w can be calculated from the monolayer thickness of water molecules on the particles surface provided the monolayer surface density of water molecules is known. For NaCl the surface density of adsorbed water molecules is usually assumed to be 6.4×10^{14} cm^{-2}, which equals the surface density of ion pairs calculated for the NaCl(001) face. This would give a slightly smaller molar volume than that of liquid water. However, the molar volume of water on ammonium sulfate is unclear. Furthermore, the surface tension of the adsorbed layer may differ considerably from that of pure water. We therefore treat the product σv_w as an adjustable parameter as we fit the adsorption isotherms to the measured data.

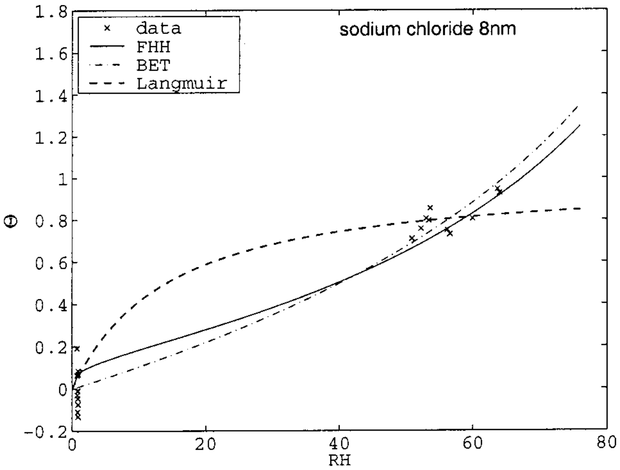

Figure 1. Measured adsorption and fitted isotherms for NaCl, dry diameter 8 nm.

Note that at the limit of infinite layer thickness the values of the molar volume and the surface tension of course have to approach the bulk values, so strictly speaking the Kelvin equation parameters are not constants. However, in practice we have to ignore this fact because we have no way of assigning an adsorption layer thickness dependence to the molar volume and surface tension.

An additional complication arises because of the cubic shape of the sodium chloride particles. Relative to a spherical particle, the vapor pressure of adsorbed water is reduced on the flat crystal faces, but on the other hand, it is increased on crystal edges. It can be shown[18] that the Kelvin equation applicable to crystal-shaped particles is similar to eq 7 with the exception that the radius of the sphere is replaced by a crystal dimension, which in the case of cubic particles is half of the length of the side of the cube. We thus replace $(r + t)$ in eq 7 by $0.806(r + t)$ (=0.5 times the side length of a cube having the same volume as the sphere) when calculating the Kelvin correction for NaCl particles.

Results

The coverages Θ calculated from the measured growth factors for the NaCl particles are presented in Figures 1−3 together with fitted adsorption isotherms. The 10 nm data showed relatively large scatter. It appears that a subset of the data, measured during a day different from those for the rest of the data, may exhibit a systematic error of the order of 0.4Θ. This corresponds to a growth factor of 0.015, which is about the same as the accuracy of the measurement. Such a systematic error may for example be due to inaccuracy of the flow measurements. The experimental setup consisted of a number of flow controlling units of various types. These controllers were calibrated prior to the experiments using a bubble flow meter. However, as the flow rate is sensitive to environmental parameters, such as temperature, pressure, and humidity, it is possible that measurements conducted during different days include a systematic error of the magnitude mentioned. To track the potential sources of the inaccuracy, we examined the atmospheric pressure during the measurement period. It appeared that the subset of data that indicated smaller values was measured during a low-pressure period and the pressure

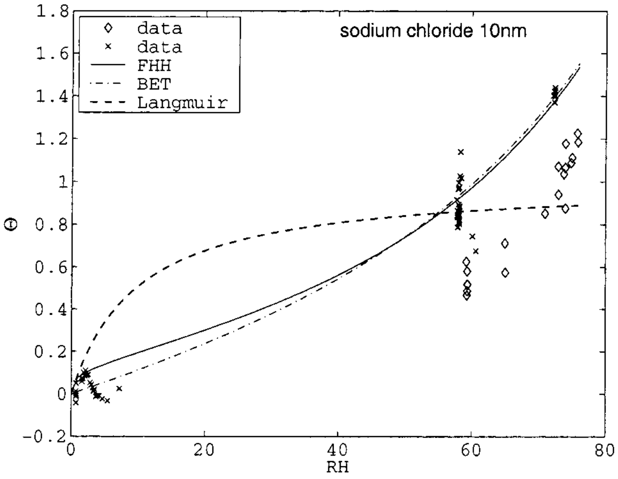

Figure 2. Measured adsorption and fitted isotherms for NaCl, dry diameter 10 nm. The data points marked with diamonds were not used in the adsorption isotherm fitting.

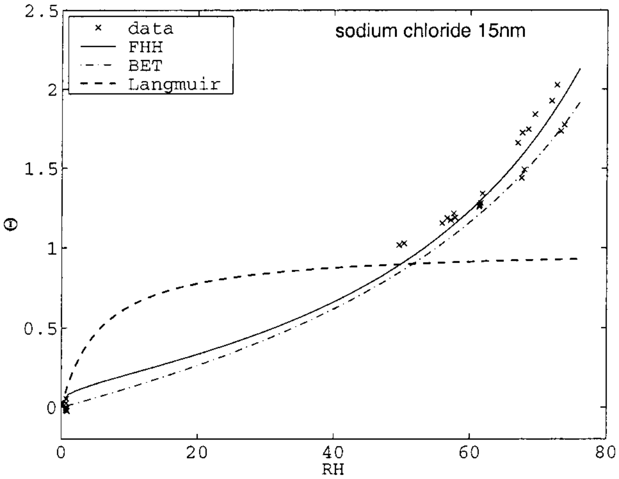

Figure 3. Measured adsorption and fitted isotherms for NaCl, dry diameter 15 nm.

TABLE 1: Constants for Different Isotherms

		NaCl	$(NH_4)_2SO_4$
Langmuir	c	1.68	0.15
	σv_w	7.70×10^{-6}	2.52×10^{-6}
BET	c	1.45	2.32
	σv_w	1.43×10^{-6}	3.36×10^{-6}
FHH	A	0.91	0.68
	B	0.67	0.93
	σv_w	2.08×10^{-6}	1.92×10^{-6}

decreased about 50 hPa over the 12 h measurement period. This finding gives a potential source of inaccuracy and affects the precision of the measurements. Typically the precision is of the order of 1% or better for determination of the size change, but the pressure changes during this period reduce the precision to about 2%.

As noted above, the primary goal of the experiments was to measure growth factors of deliquesced particles, which are of the order of 1.4−2, and therefore, we did not pay major attention to the scatter of the magnitude of 0.02 during the experiments. Furthermore, the data used in this study were measured at RH range below the deliquescence and lay therefore outside the original RH range of main interest. Due to the suspected error, the data marked with diamonds in Figure 2 was not used in the adsorption isotherm fitting process.

The fitted isotherm constants are presented in Table 1. It can be seen from Figures 1−3 that both the FHH and BET isotherms fit the data relatively well. The assumption behind the Langmuir isotherm is that the maximum surface coverage is one monolayer, and therefore, its failure at high RH's was expected. However, there is essentially no data at relative humidities between 10 and 50%, so we cannot conclude whether the Langmuir or the two other isotherms perform better at this region.

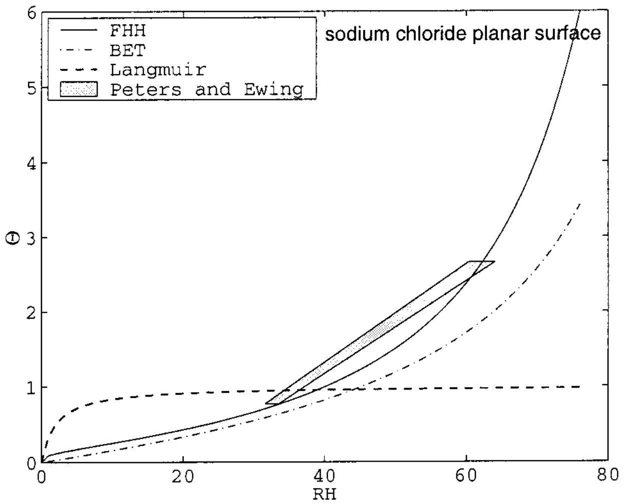

Figure 4. Isotherms calculated for a planar NaCl surface.

The same isotherms were calculated for a planar surface by applying the isotherm constants from Table 1, and they are presented in Figure 4. The shaded area represents the measurements by Peters and Ewing (the range of relative humidities shown for their experiments results from the slightly different measurement temperatures they have reported in refs 2 and 4). It can be seen that the FHH isotherm is rather close to the Peters and Ewing values, whereas the BET isotherm, which has one constant less and is therefore not as flexible, deviates somewhat at higher coverages. The values for the fitted product σv_w shown in Table 1 are quite different for each isotherm. If we calculate v_w from the surface density and monolayer thickness, we obtain $\sigma = 0.080$ N/m for the BET isotherm and $\sigma = 0.116$ N/m for the FHH isotherm, whereas the surface tension of water is 0.072 N/m. It would be possible to fit the FHH isotherms shown in Figures 1−3 to the measurement data using the liquid water value of σv_w; however, this would significantly deteriorate the agreement between the calculated planar isotherm and the data of Peters and Ewing.

Figures 5−8 show the measurement values and the fitted isotherms for $(NH_4)_2SO_4$. With ammonium sulfate, it was not possible to obtain proper fits if all the three data sets were used. Thus, the fits shown in Figures 5−8 are based on the 8 and 15 nm data sets only. The 10 nm data shown in Figure 6 would have to be shifted upward by about 0.4Θ in order to match the data with the calculated 10 nm FHH isotherm. There may be a similar systematic error in the 10 nm ammonium sulfate data as in the subset of the 10 nm sodium chloride data discussed above. We examined the atmospheric pressures recorded during the measurement period. The pressure was low during the day the 10 nm measurements were carried out as it was during the NaCl measurements shown in Figure 2 as diamonds. However, the pressure stayed very stable over the 12 h period and, indeed, the data has much less scatter compared with NaCl data. In any case, the disagreement between the 10 nm data set with the 8 and 15 nm data sets reduces the reliability of the fitted isotherms and the extrapolated flat surface isotherm of Figure 8.

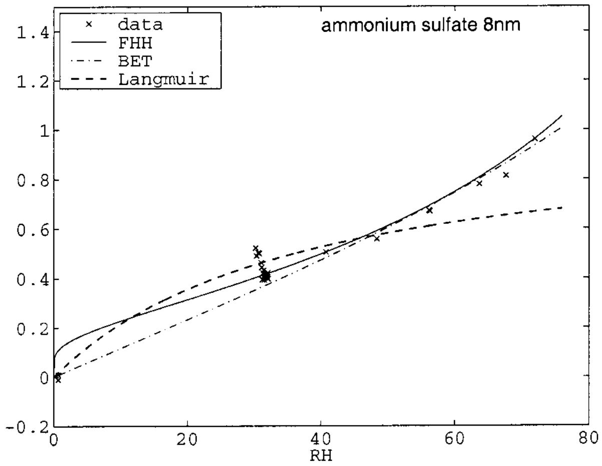

Figure 5. Measured adsorption and fitted isotherms for $(NH_4)_2SO_4$, dry diameter 8 nm.

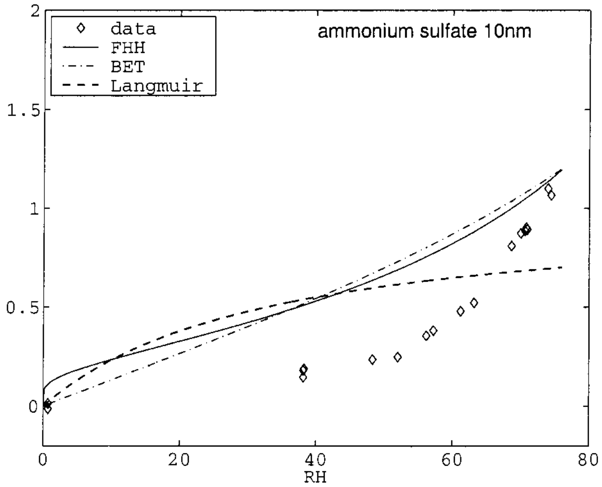

Figure 6. Calculated isotherms for $(NH_4)_2SO_4$, dry diameter 10 nm. The measurement data (diamonds) were not used in adsorption isotherm fitting.

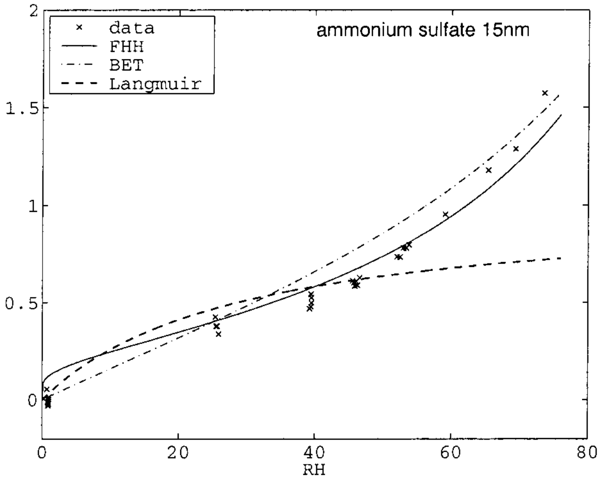

Figure 7. Measured adsorption and fitted isotherms for $(NH_4)_2SO_4$, dry diameter 15 nm.

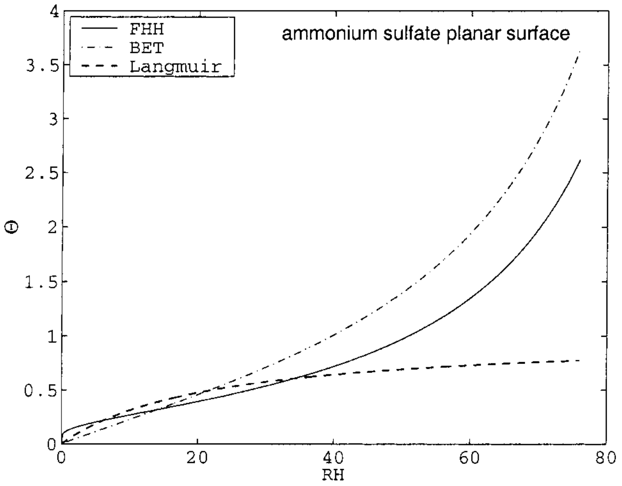

Figure 8. Calculated isotherms for planar $(NH_4)_2SO_4$ surface.

Both the BET and FHH isotherms fit the 8 nm ammonium sulfate data reasonably (Figure 5), but the FHH isotherms seems to perform somewhat better with 15 nm particles (Figure 7). The 15 nm data indicates that the FHH isotherm performs rather well also at relative humidities below 40%; however, with ammonium sulfate the Langmuir isotherm is relatively closer to the FHH isotherm than with sodium chloride, and it is difficult to conclude which isotherm gives more accurate results at low RH's.

At the planar limit (Figure 8) the BET and FHH extrapolations give rather different results. This is due to the very different values of the Kelvin equation parameter σv_w. The BET product of surface tension and molar volume given in Table 1 is about 160% higher than that for liquid water, whereas the FHH value exceeds the liquid water value by 50%. On the basis of the 15 nm fits, the FHH extrapolation would appear somewhat more reliable. However, further adsorption measurements are required for definitive conclusions.

The planar isotherms shown in Figures 4 and 8 indicate that several monolayers of water are adsorbed on sodium chloride and possibly also on ammonium sulfate in the vicinity of their deliquescence relative humidities (75.3% and 79.9%, respectively). However, the isotherms may lose accuracy because of dissolution effects as the adsorbed layer becomes thick.

Conclusions

The measurement presented in this paper showed that UF-TDMA is capable of determining the amount of water adsorbed on ultrafine particles; however, special attention has to be paid on the flow control of the system. The best correlation with measurements was found with the FHH equation, which was expected because it was the only one of the applied isotherms with two constants.

At a given relative humidity, the measurements show more water on larger particles, indicating that the particle curvature plays a significant role in adsorption on small aerosols. Comparison of the extrapolated flat surface NaCl adsorption isotherm with the data of Peters and Ewing[2,4] shows rather good agreement. This indicates that the Kelvin equation can be used to describe the effect of particle size to adsorption layer thickness.

It should be noted that, in the TDMA experiments, the primary measured quantity is the growth factor, and the coverages are calculated on the basis of assumptions concerning the shape of the dry particle and the thickness of a monolayer of water on the particle. Regardless of these reservations, it was found that considerable amounts of water is adsorbed both on sodium chloride and ammonium sulfate particles at relative humidities below the deliquescence point and that the adsorption is somewhat stronger with sodium chloride.

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