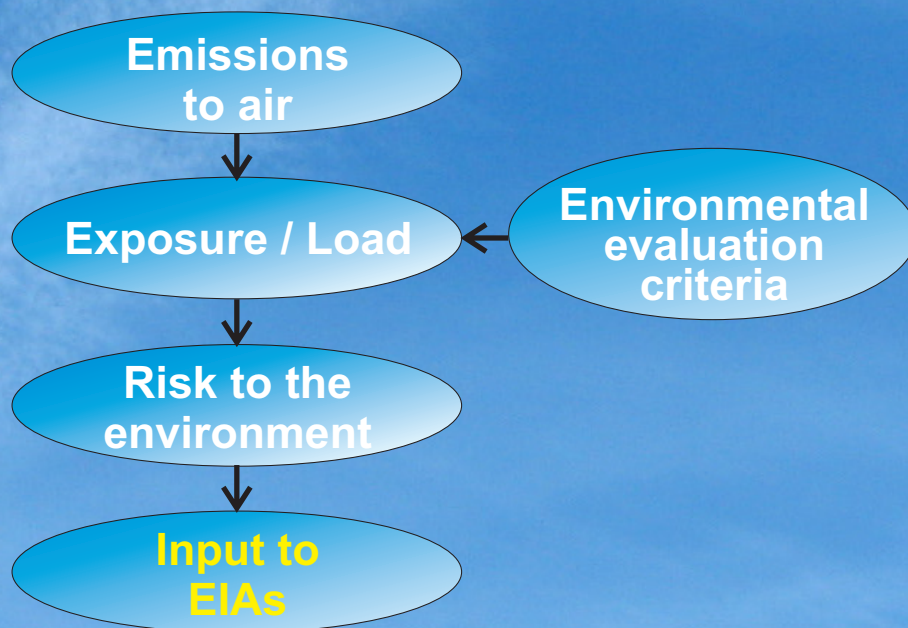




Task 5.3 Report:

Amines and Rainfall: Impact of Amines on Rainfall From Plume Clouds

Phase I: CO₂ and Amines Screening Study
for Environmental Risks



Norwegian Institute
of Public Health



Norwegian Institute
for Air Research



Norwegian Institute
for Nature Research



Norwegian Institute
for Water Research



University
of Oslo

NILU: OR 74/2008

NILU: OR 74/2008
REFERENCE: N-108068
DATE: MARCH 2009
ISBN: 978-82-425-2043-2 (print)
978-82-425-2081-4 (electronic)

Amines and Rainfall

Impact of Amines on Rainfall From Plume Clouds (Task 5.3)

Matthias Karl

Preface

CO₂ capture and storage (CCS) has been proposed for two Norwegian gas-fired power plants as a measure to reduce CO₂ emissions to the atmosphere. A leading technology for CO₂ capture is through the use of amines. The *CO₂ and Amines Screening Study Project* began with *Phase I* in May 2008. The project was initiated by the Norwegian Institute for Air Research (NILU) based on the results of an expert meeting in October 2007, and discussions with the Norwegian Pollution Control Authority (SFT). The expert meeting and the following Phase I project is based upon the concern that the emissions from CO₂ capture using amines could be potentially harmful to the environment and human health, and that the existing information regarding these subjects were quite limited, thus demanding further examination and analysis.

The project was graciously sponsored by the following:

- Gassnova SF (CLIMIT)
- Statoil Hydro ASA
- Shell Technology Norway AS

The following institutes participated in the project:

- Centre for Theoretical and Computational Chemistry (CTCC) Department of Chemistry at the University of Oslo, responsible for the theoretical study on the atmospheric photo-oxidation of selected amines (Task 3).
- The Norwegian Institute of Public Health (FHI), responsible for the effects to human health (Task 7).
- Norwegian Institute for Nature Research (NINA), responsible for the effects to terrestrial ecosystems (Task 8).
- Norwegian Institute for Water Research (NIVA), responsible for the effects on freshwater ecosystems (Task 9).
- Norwegian Institute for Air Research (NILU), responsible for project management/coordination, including the chemical screening report, models report, worst case study report, and the summary report (Task 4, 5, 6, and 10).

The project sponsors comprised the Steering Committee, which gave useful guidance to the project and its administration. The project sponsors function within the Steering Committee also gave them an active role in reviewing all project reports and documentation.

Contents

	Page
Preface	1
Summary	3
1 Introduction	5
2 Emission estimate	6
3 From particles to cloud droplets	6
4 Growth of cloud droplets	13
5 Formation of rain	14
5.1 Collision/coalescence	14
5.2 Ice crystal formation and ice processes	15
5.3 Amount of rainwater	17
6 Worst case scenario	18
7 Further improvements and recommendations	19
8 References	21

Summary

Growth of droplets by water vapour condensation is a very effective mechanism for the initial growth of submicron droplets formed from small particles in air. This process reaches an equilibrium within a few minutes. The growth of water droplets in the atmosphere strongly depends on their surface tension. An important effect of amines is to lower the surface tension. Thus amines enhance the probability that very small water droplets can grow to cloud droplet size (10-20 μm) and cause cloud formation in the plume of the CO_2 capture plant at a lower ambient humidity. Added amines promote the formation of supercritical droplets that can cause rainfall from the plume; thus amines act as a trigger of rain. Simple equilibrium model calculations for Monoethanolamine (MEA) show that in the absence of amines, no droplets of a given droplet size distribution become activated at 0% supersaturation (i.e. 100% relative humidity). Within the plume, the atmospheric gas phase concentration of MEA will determine the actual amount of activated cloud condensation nuclei (CCN). If sufficient humidity is available in the surrounding air, the activated droplets can continue to grow into rain drops; this may be the case during cold spells with fog events.

As a worst case, the saturation ratio for a given aerosol population was calculated for 10 ppbv MEA. In this case, the total aerosol droplet population would become activated at 99% relative humidity inside the plume. Given sufficient water vapour content, this situation would lead to a rapid formation of a larger droplets containing dissolved amine.

In the atmosphere, growth from cloud droplet sizes (10 to 20 μm) to rain drop sizes (several hundred μm to 2 mm) not only occurs by water vapour condensation but also by coalescence of droplets and ice-related processes. The possible influence of amines on ice nuclei formation is discussed in this report. Though it cannot be fully excluded, it is unlikely that the amines used in the CO_2 capture process have an inhibiting effect on ice crystal formation.

The equilibrium model approach presented in this study has several limitations:

- 1) The mass transfer of a gas phase species through the air-water interface of droplets is described as gas phase/water equilibrium;
- 2) The effect of ionic strength in water droplets is not taken into account;
- 3) The influence of amines on surface tension is estimated, and not from experimental data on aqueous amine solutions;
- 4) Finally, the occurrence of rainfall from the plume cloud also depends on the temperature, specific humidity and meteorological stability of the boundary layer.

Amines enhance the probability that very small water droplets can grow to cloud droplet size and cause rain formation in the plume of the CO_2 capture plant. Rain drops falling from the plume cloud contain dissolved amines and might cause effects on buildings, materials and human health in the vicinity of the CO_2 capture

plant. It is thus recommended to continue research on effects of amines on rainfall from plume clouds of CO₂ capture facilities. In a next step a microphysical aerosol/cloud model should be developed to study the temporal evolution of droplets based on the Köhler equation. In addition it is recommended to carry out experimental work in a fog chamber to evaluate the change of droplet characteristics through the addition of amines.

To predict the possibility of rainfall and the amount of rain water for certain meteorological conditions the microphysical aerosol/cloud model should be coupled with a meteorological dispersion model.

Amines and Rainfall

Impact of Amines on Rainfall From Plume Clouds (Task 5.3)

1 Introduction

Aqueous solutions of amines are used for removing carbon dioxide (CO₂) from the flue gas of power plants. Aqueous solutions as such can only weakly dissolve CO₂ or other gases from a gas stream. Amines act as a weak base, and neutralizes the acidic compounds (carboxylic acid, CO₂-H₂O) dissolved in the solution and turns the neutral molecules into the ionic form (i.e., bicarbonate ions, HCO₃⁻ and carbonate, CO₃²⁻). In the absorber unit of a CO₂ capture plant, amines help to keep the CO₂ gas dissolved in the gas-scrubbing solution. During this process a certain fraction of amines escape from the absorber and are emitted to the atmosphere. Amines in the emissions of the absorber unit will be partly contained in water droplets generated by the scrubber and in fresh liquid droplets that formed after the flue gas leaves the stack. The emissions can also be as gasses. Monoethanolamine (MEA) is the most studied solvent for the removal of CO₂ from flue gases. Its rate of absorption of CO₂ is very high. MEA is used as a model amine compound in this report.

Amines, like Monoethanolamine (MEA), are used as surface active agents in other industrial applications. Thus their ability to lower the surface tension of water is well known. The growth of a liquid droplet in the atmosphere strongly depends on the surface tension. The surface tension and the partial water vapour pressure will decide the droplet size. The lower the surface tension, the larger the droplet can get. Cloud droplets will normally be small and will not grow into rain drops. When adding amine, the droplets can grow larger and can exceed a critical size. Aerosol particles then grow into cloud droplets at certain levels of humidity, this process is known as activation. These particles will act as cloud condensation nuclei (CCN). There will always be sufficient small particles to form the initial cloud droplets. However, adding amines to small water droplets will lower their surface tension and in consequence allow for growth out of the equilibrium state at lower humidity. Thus amines enhance the probability that very small water droplets can grow to cloud droplet size (10-20 µm) and cause cloud formation in the plume of the CO₂ capture plant. Because of the reduction in the surface tension, cloud droplets can grow to larger droplets that can form rain drops either by growth through condensation or by collision. Finally, the droplets will reach the size of rain drops. If the falling rain drops become large enough (about 300 µm) they will be able to reach the ground.

Rain drops falling from the plume cloud contain dissolved amines. Amines are corrosive, smelly, and effect human health; thus rain drops containing amines might cause effects on buildings, materials and human health in the vicinity of the CO₂ capture plant.

2 Emission estimate

The estimated emission of amines from the CO₂ capture facility is 50-200 tonnes per year (75 tonnes per year on average). Assuming a plume exit velocity of 15 ms⁻¹ and a chimney outlet area of 1.2 m² the emission rate of amines is 2.8 g/s (on the average). In the following calculations, MEA is used as a representative for amine compounds used for CO₂ separation from the flue gas (MEA properties see Table 1).

Table 1: Properties of Monoethanolamine (MEA) employed in this study.

Molar weight M (gmol ⁻¹)	Henry coefficient kH (Matm ⁻¹)	Acidity constant pKa (298K)	Reaction rate constant K(MEA+OH) (cm ³ s ⁻¹) ¹
61.08	6.2x10 ⁶	9.6	2.8x10 ⁻¹¹

¹ Rate constant value taken from the reaction of Aminomethylpropanol (AMP) with OH.

With the given emission rate, the initial molar concentration of MEA in the plume from the CO₂ capture plant is calculated to be 2.5x10⁻⁹ moles per cubic centimetre air. This corresponds to a mixing ratio of about 60 ppmv at 298 K. As the plume leaves the stack, MEA starts to react with the atmospheric hydroxyl radicals (OH) and gas phase MEA concentrations decrease. At steady state the MEA concentration equals the ratio of emission rate (in cm³ s⁻¹) to the loss rate by OH reaction (in s⁻¹). Assuming a steady state OH concentration of 2x10⁶ molecules per cm³ and using the rate constant of the reaction of Aminomethylpropanol (AMP) with OH which is 2.8x10⁻¹¹ cm³ s⁻¹, the loss rate for MEA reacting with OH is 5.6x10⁻⁵ s⁻¹. The MEA steady state concentration is thus 3.2x10¹¹ molecules cm⁻³, corresponding to 13 ppbv. For the further discussion of the impact of amines on cloud droplet formation MEA mixing ratios of 10 ppbv or less are used in order to apply equilibrium assumptions for the partitioning between gas phase and aqueous phase and to treat the aerosol water as an ideal solution. Considering the entrainment of ambient air into the plume air, the use of lower MEA mixing ratios is a more conservative estimate of the amine concentration inside the plume. However, it should be kept in mind that the actual gas phase concentration of amines at the time before the plume leaves the chimney is expected to be 3 orders of magnitude higher.

3 From particles to cloud droplets

Figure 1 depicts the processes involved in the evolution of a rain drop starting with a very small dry particle. The initial step is the formation of very small dry particles of sizes below 10 nm. These particles form immediately when the flue gas leaves the stack, either by homogeneous nucleation of the ternary mixture H₂SO₄-NH₃-H₂O or by the gas phase reaction between gaseous sulphuric acid and ammonia. Though SO₂ is partly removed from the flue gas by the SO₂ scrubber, a certain fraction of SO₂ will pass the scrubber (about 2 ppmv) and is oxidised in

the atmosphere by hydroxyl radicals (OH) to sulphuric acid. The gas phase reaction with ammonia (NH₃) yields solid ammonium sulphate particles. Ammonia, a degradation product of the processed MEA, is present in the plume at high concentrations (about 8 ppmv). Thus, the plume will contain large numbers of initially formed small ammonium sulphate particles. In the absorber unit, temperature is 55°C and relative humidity is very high, presumably 120%. For the calculations presented here, a temperature of 298 K and a relative humidity (RH) of 100% are used.

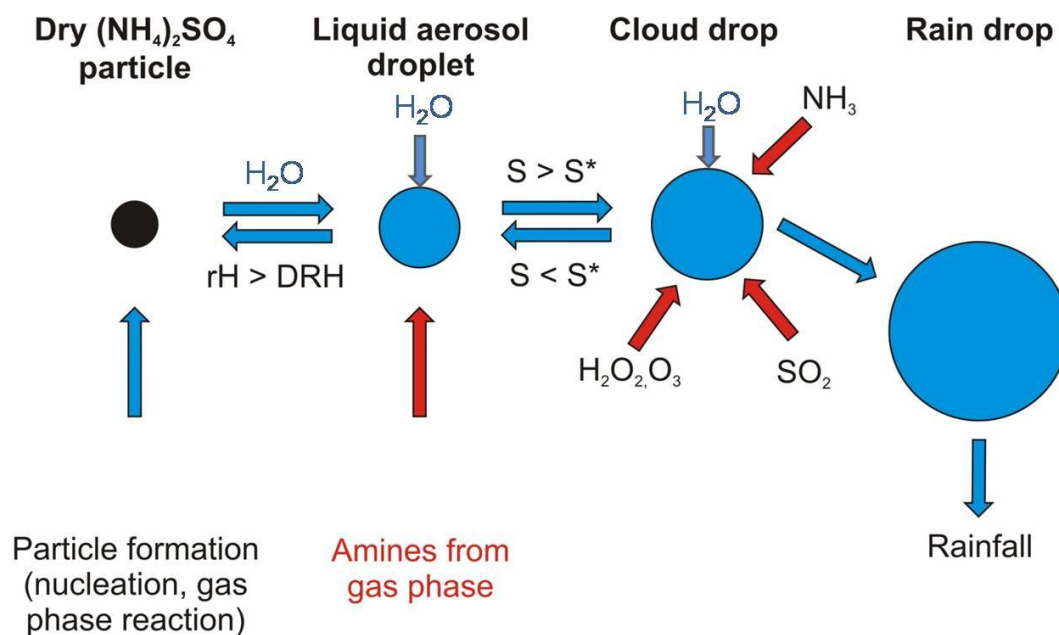


Figure 1: Processes involved in the growth from a nanometre sized dry particle to a rain drop (S denotes saturation ratio and S^* denotes critical saturation ratio).

When the deliquescence point (deliquescence relative humidity, DRH) is reached, the solid particles spontaneously absorb water, producing a saturated aqueous solution. Further increase of the relative humidity leads to additional water condensation onto the salt solution to maintain the thermodynamic equilibrium. For ammonium sulphate ((NH₄)₂SO₄), a hygroscopic inorganic salt, the DRH is at 80% RH (Figure 2). The DRH for ammonium sulphate is practically constant within the temperature range of interest. In the following it is assumed that aerosol particles have grown to liquid water droplets of the accumulation mode size at 100% RH, and neglect the sulphate mass fraction in the water droplets.

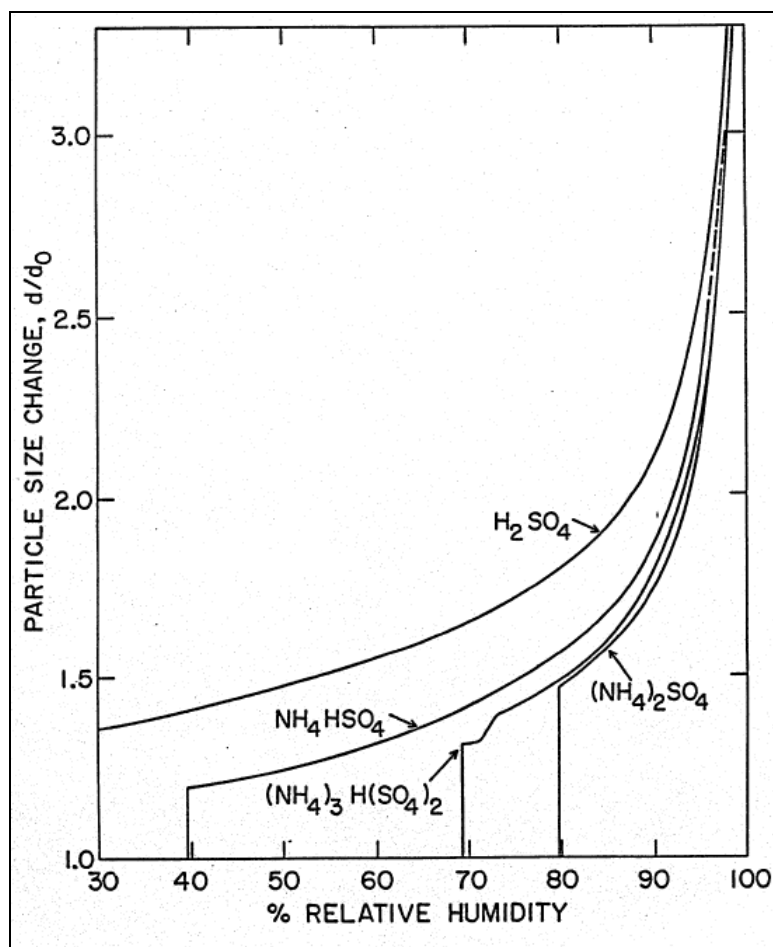
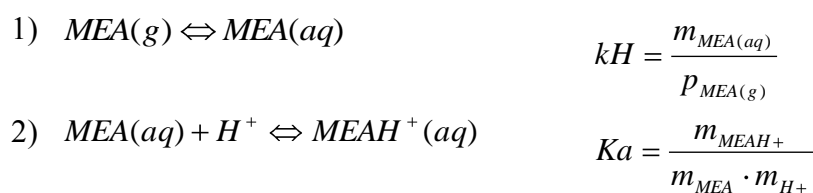


Figure 2: Sulphate particles size change due to deliquescence, taken from Tang, 1980.

A thermodynamic equilibrium is assumed for the partitioning of amines between the gas phase and the aerosol water. Mass transfer through the air-water interface may limit the uptake of gases to the aerosol particle, but is not considered in the following. Since the initial water droplets are small, it can be assumed that the dissolved amines are distributed instantaneously throughout the whole droplet. Thus Henry's Law can be applied to calculate the equilibrium concentration of dissolved amines in aerosol particles. In the compilation of Henry coefficients for inorganic and organic compounds by R. Sander (1999) (<http://www.mpch-mainz.mg.de/~sander/res/henry.html>), the Henry's Law constant (kH) of MEA is given with a value of $6.2 \times 10^6 \text{ M atm}^{-1}$. Therefore gaseous MEA is very soluble in water, a million times more than SO_2 . In neutral water ($\text{pH}=7$), MEA will readily dissociate into MEA^+ :



The effective Henry coefficient is thus:

$$kH^* = kH \cdot \left(1 + \frac{Ka}{[H^+]}\right) \quad (1)$$

The pKa of MEA is 9.6 at 298 K. At pH = 7, $kH^* \cong kH$. Using $kH = 6.2 \times 10^6 \text{ M atm}^{-1}$, the molality of dissolved amines in the aerosol water is $6.2 \times 10^{-2} \text{ mol kg}_{\text{H}_2\text{O}}^{-1}$ for a mixing ratio of 10 ppbv of MEA in the plume.

A key aspect of aqueous aerosols is their curved surface. The equilibrium vapour pressure over a curved surface is always larger than the corresponding vapour pressure over a flat surface. When a curved interface exists between air and water, as in a small droplet, there are fewer molecules immediately adjacent to a molecule of water on the surface than when the surface is flat. Therefore, it is easier for the molecules of a small droplet to escape into the vapour phase and the vapour pressure over the curved surface will be greater. Surface tension plays an important role in the curvature effect. Smaller droplets have a tighter curvature. The greater the surface tension of a particle against air, the more likely a water molecule escapes from the surface and the greater the saturation vapour pressure. The curvature effect S_{Kelvin} , i.e. the relative increase of the vapour pressure over a droplet with radius r compared to over a flat surface is described by the Kelvin equation,

$$S_{Kelvin} = \exp\left(\frac{2 \cdot \sigma_p \cdot M_p}{r_i \cdot R \cdot T \cdot \rho_p}\right) \approx 1 + \frac{2 \cdot \sigma_p \cdot M_p}{r_i \cdot R \cdot T \cdot \rho_p} \quad (2)$$

σ_p is the average particle surface tension (g s^{-2}), ρ_p the average density of particles (g cm^{-3}), M_p is the molecular weight of the average particle (g mol^{-1}), r_i is the particle radius in the actual size bin (cm), R the universal gas constant ($8.31451 \times 10^7 \text{ g cm}^2 \text{ mol}^{-1} \text{ K}^{-1}$) and T is ambient temperature (K). The given aerosol population is treated as accumulation mode water droplets. The lognormal parameters of the chosen aerosol size distribution and other initial parameters are given in Table 2.

Table 2: Parameters of the aerosol size distribution for the lognormal accumulation mode that is used in the study and some meteorological parameters of the plume.

Accumulation mode size distribution			Meteorology	
N (cm^{-3})	D_p (μm)	Width σ	Temperature (K)	Rel. Humidity (%)
1.3×10^4	0.09	2.00	298.15	100.0

Water has a relatively high surface tension, because of strong hydrogen bonds. Amines are surface-active compounds (surfactants) and the effect of dissolved amines is to lower the surface tension of the water droplets. Fachini et al. (1999) have studied the influence of organic solutes on the surface tension and on the

activation of aerosols to CCN. From laboratory measurements of surface tension in sampled cloud and fog water, they obtained the following empirical function of the particle surface tension by fitting the Szyszkowski-Langmuir equation to their data:

$$\sigma_p = \sigma_w - 0.0187 \cdot T \ln(1 + 628.14 \cdot m_C) \quad (3)$$

Where σ_w is the surface tension of water (g s^{-2}), and m_C the molality of carbon dissolved in water ($\text{mol C kg}_{\text{H}_2\text{O}}^{-1}$). MEA and other alkanolamines are organic compounds and have been found experimentally to lower the surface tension of water (Aguila-Hernández et al., 2001). In this approach the equation (3) is used to calculate the particle surface tension for given molality of carbon from dissolved MEA.

A second factor that affects the saturation vapour pressure is that of dissolved solutes (dissociated or undissociated), the solute effect. When a solute dissolves in solution, the saturation vapour pressure of the solvent is reduced. For a pure involatile solute (not evaporating), the vapour pressure is zero. By adding molecules of a solute to the solution, solvent molecules on the droplet surface are replaced by solute molecules. Since the total vapour pressure over the solution is the sum of the vapour pressures of the solvent and the solute, the total vapour pressure over the solution will be less than over the pure solute alone. From Raoult's Law the solute effect S_{Raoult} over a dilute liquid water solution is described by:

$$S_{Raoult} \approx 1 - \frac{3 \cdot m_s \cdot \nu \cdot M_w}{4\pi \cdot r_i^3 \cdot \rho_w \cdot M_s} \quad (4)$$

With m_s being the mass of solute in the droplet (g), M_w the molar weight (g mol^{-1}) and ρ_w the density of water (g cm^{-3}). M_s is the molar weight of the solute (g mol^{-1}). The van't Hoff factor ν describes the number of moles of ions produced per mole of solute, with $\nu = 2$ for MEA. While the curvature effects increases the vapour pressure over small droplets, the solute effect decreases it. Since MEA will be completely dissolved in the aerosol droplets, MEA is a solute and addition of MEA will decrease the vapour pressure. The solute effect affects primarily small particles, since small particles have a higher concentration of solute than the larger particles.

Kelvin and Raoult describe competing effects: while the curvature tends to increase the saturation vapour pressure over small water droplets, the solute tends to decrease it. The combination of the Kelvin and Raoult effect results in the Kohler equation. The Kohler equation relates the saturation vapour pressure of water over a curved surface containing solute to that over a flat surface without solute:

$$S' \cong 1 + \frac{2 \cdot \sigma_p M_p}{r_i \cdot R \cdot T \cdot \rho_p} - \frac{3 \cdot m_s \cdot \nu \cdot M_w}{4\pi \cdot r_i^3 \cdot \rho_w \cdot M_s} \quad (5)$$

In Figure 3, the equilibrium saturation ratio, S' , is shown for a gas phase concentration of 3 ppbv of MEA in the plume for the lognormal accumulation mode aerosol and other parameters from Table 2, together with the curves of S_{Kelvin} (blue line) and S_{Raoult} (red line) for the given amine. Supposed, the ambient saturation ratio is $S=1.000$ (RH = 100%), or in other words super saturation is 0%, then a particle with a radius of $0.04 \mu\text{m}$ will start to grow by adding water molecules, and S' increases along the equilibrium saturation curve (green line), as long as ambient $S > S'$. At maximum equilibrium saturation ratio, the critical saturation ratio S^* is reached. The corresponding radius is the critical radius r^* . Particles starting with a radius smaller than the critical radius cannot grow further to cloud-drop size unless the ambient saturation ratio exceeds the critical saturation ratio. Particles with initial sizes larger than the critical radius can activate if $S > S'$ over these droplets. Therefore a droplet starting with a radius $0.1 \mu\text{m}$ can grow freely into a cloud droplet at 0% super saturation.

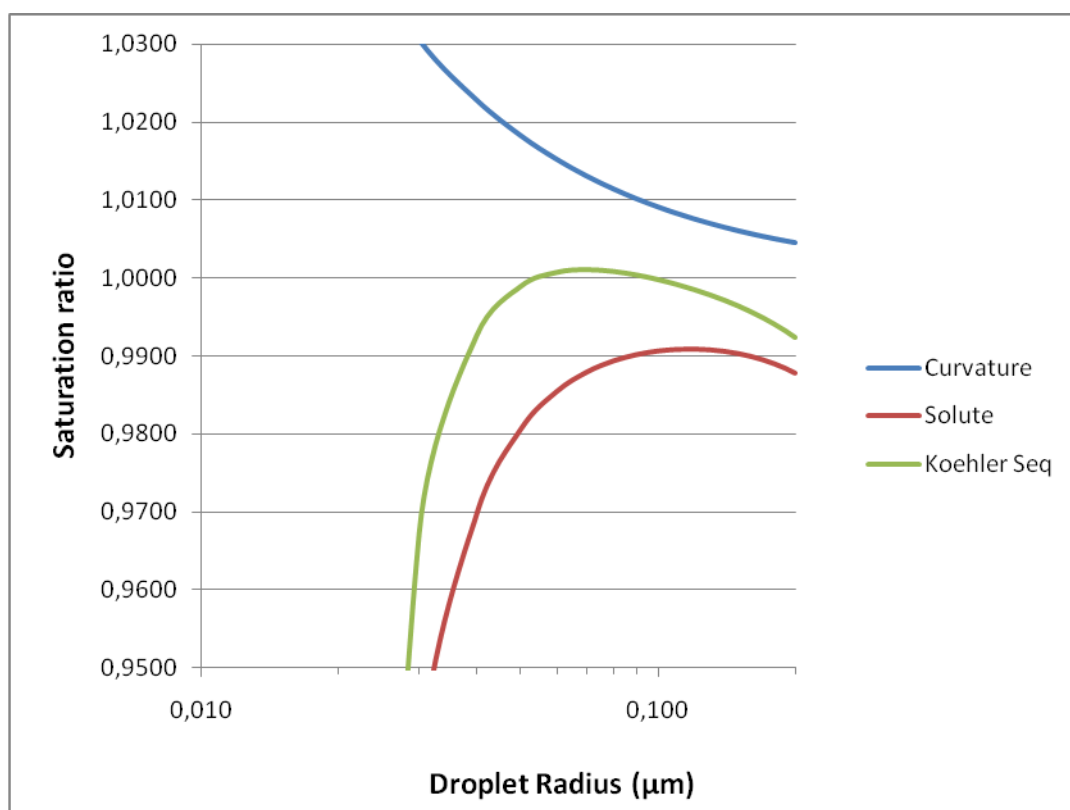


Figure 3: Saturation ratio over accumulation mode aerosol droplets (see Table 2) as function of the wet radius for 3 ppbv of MEA in the gas phase of the plume.

The critical radius for growth to cloud droplets and the critical saturation ratio can be calculated using:

$$r^* = \sqrt{\frac{3b}{a}} \quad S^* = 1 + \sqrt{\frac{4a^3}{27b}}$$

with

$$a = \frac{2 \cdot \sigma_p \cdot M_p}{R \cdot T \cdot \rho_p} \quad b = \frac{3 \cdot m_s \cdot \nu \cdot M_w}{4\pi \cdot \rho_w \cdot M_s} \quad (6)$$

The effect of amines on the Kohler equilibrium saturation curve is shown in Figure 4. In this figure the Kohler curves for a) no MEA added, b) 1 ppbv, and c) 10 ppbv MEA are plotted for the given aerosol population. With no amines in the gas phase the saturation ratio of the water droplets corresponds to the equilibrium saturation ratio due to the Kelvin effect alone.

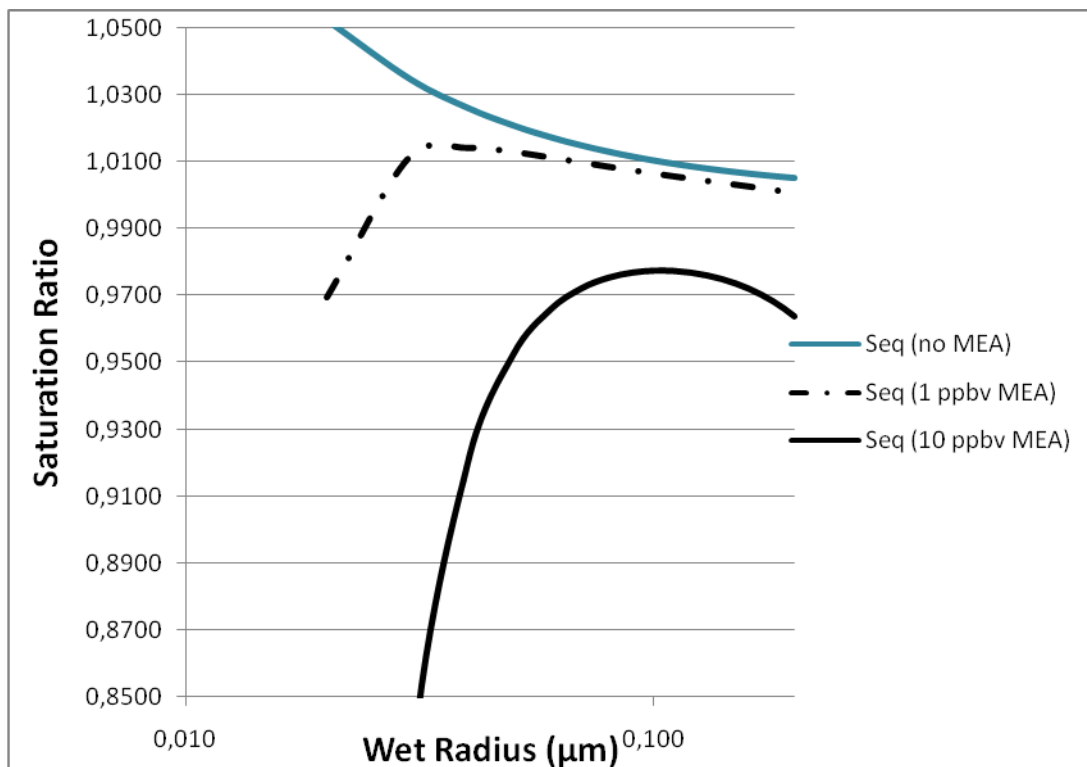


Figure 4: Saturation ratio over accumulation mode aerosol droplets (see Table 2) as function of the wet radius for a) no MEA (cyan line), b) 1 ppbv MEA (dash-dotted black line), and c) 10 ppbv MEA (solid black line).

It should be noted, that the solute effect of dissolved sulphate in the droplets is not considered. If MEA is not present, none of the droplets in the accumulation mode becomes activated at 0% super saturation. With a gas phase concentration of 1 ppbv MEA the critical radius is 0.04 μm and at 1% super saturation, droplets with an initial radius larger than 0.07 μm can become activated. At 10 ppbv MEA the solute effect dominates and all droplets in the accumulation mode will be activated. Thus between 1 and 10 ppbv MEA the influence of the amines on the surface tension is most decisive for the activation barrier and the relation between the ambient saturation ratio and the saturation ratio over the droplets will determine the amount of activated CCN.

The respective thresholds for the activation of aerosol particles to CCN (activation diameter) at 0.1 ppbv and 1 ppbv MEA are shown in Figure 5 for a given super

saturation of 0.1%. The activation diameter is reduced from 0.2 μm at 0.1 ppbv MEA down to 0.14 μm at 1 ppbv MEA and the number concentration of CCN increases from 600 cm^{-3} to 1380 cm^{-3} .

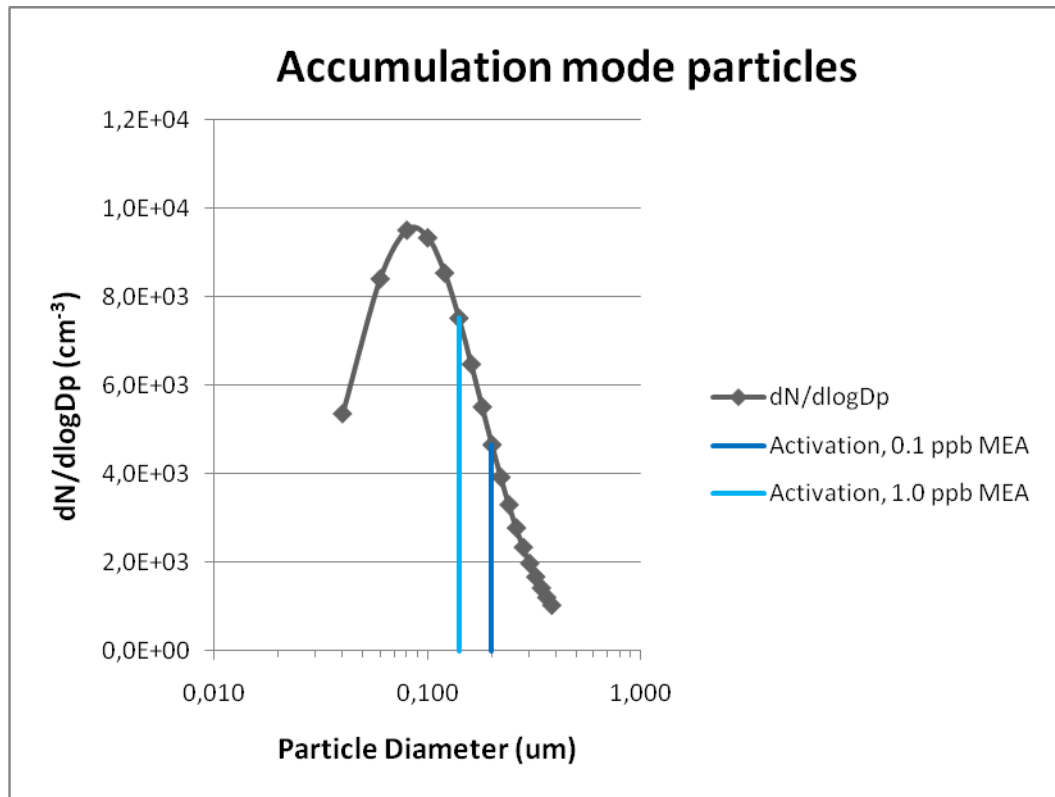


Figure 5: Activation diameters for the droplets of the given accumulation mode size distribution at 0.1% super saturation. Dark blue line denotes the activation diameter at 0.1 ppbv MEA of 0.2 μm and light blue line denotes the activation diameter at 1 ppbv MEA of 0.14 μm .

4 Growth of cloud droplets

Growth of droplets by water vapour condensation according to the principles outlined in chapter 3 is a very effective mechanism for the initial growth of aerosol particles from sub micrometre sizes to 10-20 μm sizes which all occurs within minutes. However the further growth of a droplet is a slow process. For instance, about one hour is necessary under a constant super saturation of 1% for droplets to grow to 100 μm . Thus the growth of droplets merely by condensation of water vapour is only effective until the droplet distribution reaches sizes up to 10 or 20 μm . Moreover, surrounding air will entrain into the rising air parcel from the plume and thus diluting the liquid mass content of the plume cloud.

The growth equation for water vapour condensation on droplets considering the solution and curvature effects is,

$$r \frac{dr}{dt} = \frac{(S-1) - \frac{a}{r} + \frac{b}{r^3}}{[F_k + F_d]} \quad (7)$$

Where a and b are from equation (6), F_k represents a thermodynamic term associated with heat conduction and F_d is a term associated with vapour diffusion.

In clouds, soluble gases like SO_2 , ammonia, HNO_3 become dissolved in the cloud droplets (see Figure 1). The cloud water serves as a reaction medium for a series of aqueous phase chemistry reactions, the most important one being the transformation of dissolved SO_2 into sulphate (SVI). The formed sulphate is non-volatile and will increase the dry mass of the particulate phase after the cloud has evaporated. The result of the aqueous phase reactions is in general an increase in particle mass and size of the activated aerosols.

Droplets with a radius of $10 \mu\text{m}$ can fall only a few millimetres before they will evaporate. Only rain drops of the size larger than $300 \mu\text{m}$ can reach the ground as rainfall. For bridging the growth span between $10 \mu\text{m}$ and several $100 \mu\text{m}$ apart from the condensation of water vapour, other mechanisms like coalescence of droplets and ice-related processes are responsible. These two processes and the possible influence of amines on ice nuclei formation will be discussed in Chapter 5.

5 Formation of rain

The addition of amines promotes the formation of supercritical droplets that can cause rainfall from the plume. With the addition of amines some of the droplets in the plume will grow to supercritical size and thereby continue to grow freely. Other mechanisms like coalescence of droplets and ice-related processes assist the water droplets in growing from $10 \mu\text{m}$ size to rain drop sizes. Initially though, amines act as a trigger to activate a fraction of the liquid aerosol droplets into larger cloud droplets. In consequence these activated droplets trigger the coalescence, i.e. the collection of smaller droplets during their fall, as collector drops. Section 5.1 describes the growth of a drop by the process of collision/coalescence. In section 5.2, the mechanism of ice crystal formation and ice-related growth processes are described. The possible influence on added amines on ice-related processes is discussed in detail. Section 5.3 introduces a simple approach to determine the rain water amount that falls to the ground.

5.1 Collision/coalescence

In a cloud droplet distribution with $10 \mu\text{m}$ size droplets, the larger drops will start to fall and collect smaller droplets. Gravitational collection of droplets is the predominant mechanism in warm clouds that form rain drops (e.g. typical for tropical thunderstorms). Large drops fall faster than smaller drops, overtaking and capturing of the smaller ones that lie in their falling path. A large drop will only collide with a fraction of the smaller drops, because some are swept aside in the airstream around the large drop.

The collection efficiency describes the probability by which two particles collide and stick together to form a new and larger drop (coalesce). The growth of a falling drop of mass m as a result of the collision/coalescence can be described by,

$$\frac{dm}{dt} = \pi \cdot E \cdot (V_{t,c} - V_{t,d}) \cdot (r_c + r_d)^2 \cdot L \quad (8)$$

E is the collection efficiency, L is the liquid water content (g) of the small drops, V_t is the terminal fall speed (cm s^{-1}) of the collector drop (index c) and the smaller drops (index d), r_c is the radius of the collector drop (cm) and r_d the radius of the smaller drops. For the terminal fall speed the following approximations can be made, depending on the given size range of the falling drop:

Terminal fall speed		Size range
$V_t = k_1 \cdot r^2$	$k_1 = 1.19 \cdot 10^6 \text{ cm}^{-1} \text{ s}^{-1}$	Up to 30 μm
$V_t = k_2 \cdot r$	$k_2 = 8 \cdot 10^3 \text{ s}^{-1}$	30 μm to 0.6 mm
$V_t = k_3 \cdot \sqrt{r}$	$k_3 = 2.01 \cdot 10^3 \text{ cm}^{-1/2} \text{ s}^{-1}$	0.6 to 2 mm

(9)

Gravitational collection is the most important mechanism by which clouds form rain drops in warm clouds (clouds with temperatures above 0°C). Much emphasis thus should be given to the treatment of the collection efficiency when developing a model for studying the plume cloud.

5.2 Ice crystal formation and ice processes

Once a cloud extends to or reaches altitudes where the temperature is colder than about -12°C , ice crystals may form. Two phase transitions can lead to ice formation: 1) the freezing of a liquid droplet (homogeneous nucleation) or 2) the sublimation of water vapour onto the solid phase (heterogeneous nucleation).

Homogeneous freezing of a pure liquid droplet occurs by the formation of ice nuclei due to statistical fluctuations in the molecular arrangement of water. Droplets with size smaller than 5 μm will freeze spontaneously at a temperature of about -40°C or below. Therefore this process is only relevant for high altitudes. In the continental boundary layer the background concentrations of particles is always high enough to promote freezing at higher temperatures. In the presence of foreign material, liquid droplets can freeze at temperatures above -40°C (heterogeneous freezing).

Foreign material, like solid particles, provides a surface on which water molecules can impinge, stick, and form aggregates of an ice-like structure. The more the particle resembles the structure of an ice-crystal the more suitable it is for heterogeneous freezing. The material matching ice the closest in structure is silver iodide. A number of organic compounds however can act as ice nuclei at temperatures above -10°C , e.g. some amino acids and several aromatic compounds (Fukuta, 1966). The essential requirements for an organic compound to be efficient ice nuclei are: 1) the compound molecules should possess polar or hydrogen-bonding groups, 2) the compounds should have low solubility in water,

and c) they should be crystalline solids of reasonable high melting point (Fukuta, 1966). Since amines of the CO₂ capture process are very soluble, the second requirement is not fulfilled. Also the melting point is rather low (MEA: 10.3°C). Organic compounds that are found to be ideal ice nuclei also have one or more crystal planes matching the plane(s) of an ice crystal.

As background air containing particles entrains into the plume cloud, potential material for heterogeneous freezing becomes available. However, liquid drop formation can still occur at temperatures down to -40°C. A liquid droplet that exists below 0°C is called “supercooled” droplet. At temperatures below 0°C, supercooled droplet formation competes with ice crystal formation (e.g. by heterogeneous nucleation on background particles) for the limited amount of water available. Ice growth is favoured since the saturation vapour mole concentration over ice is less than that over liquid. The activation of particles into ice nuclei is described by the Kelvin effect, which affects the saturation ratio at equilibrium over ice,

$$S'_i \cong 1 + \frac{2 \cdot \sigma_i M_p}{r_i \cdot R \cdot T \cdot \rho_i} \quad (10)$$

In equation (10) σ_i is the average surface tension of ice (gs⁻²) and ρ_i the density of ice (gcm⁻³). The surface tension of ice varies between 100 and 110 gs⁻² which is higher than that of water and thus the saturation ratio over ice is higher than that over water for a droplet of the same size. While the dependence of the surface tension of ice on the radius of the particle is well known, there are only few studies on the dependence of the surface tension of ice on the compounds that are dissolved in the liquid droplet.

Wise et al. (2004) found in homogeneous freezing experiments that mixed solutions of ammonium sulphate and dicarboxylic acids (commonly found in organic aerosol particles) freeze at the same temperature as ammonium sulphate solutions with the same water activity. Their results suggest that dissolved organic compounds do not influence the surface tension of ice.

Dissolution of a salt like MEA lowers the vapour pressure over the solution. A direct result of this is the depression of the freezing point of water. As a consequence freezing of water droplets will start at a lower temperature than 0°C. For MEA, a salt that dissociates into two ions, the freezing point depression is 3.72°C kg mol⁻¹ in an ideal solution. For 5 ppbv MEA in air the freezing point decreases by 0.12°C. The depression of the freezing point depends on the concentration of the dissolved compound but not on the chemical nature of the dissolve compound.

It has been discussed in literature, that amines could affect the heterogeneous nucleation of ice crystals and inhibit the formation of ice nuclei. Birstein (1960) found that ammonia and various amines effectively inhibited heterogeneous nucleation of water vapour onto silver iodide crystals. Georgii (1963) concluded that the inhibition process was irreversible chemisorption of the inhibitor gas

molecules on the crystal's surface. Davis and Steele (1968) reported that the presence of isopropyl amine vapour in a cloud chamber inhibited ice crystal formation on silver iodide seed particles. In a later report by Schnell and Vali (1974) it was shown however, that most of the observed inhibition phenomena could be attributed to melting point depression. In experiments with ammonia the observed changes in the heterogeneous freezing temperature were below 2°C in most cases, and 4°C at most. Schnell and Vali suggest that there are no strong interactions between various gases and different types of nucleating materials, though a fairly significant inhibition effect was found for the higher alkenes and for isopropyl-amine. In these cases, the equilibrium saturation ratio described by equation (5) will be valid at lower temperatures and water droplets can exist as supercooled droplets.

The impact of amines on the ice-processing mechanism can be summarized as follows:

1. amines cannot act as ice nuclei themselves;
2. amines are unlikely to affect the activation of particles into ice nuclei;
3. for the expected amines concentrations, freezing point depression in water droplets is very small;
4. gas phase amines are unlikely to interact with nucleating material in the atmosphere.

It cannot be fully excluded that the amines used in the CO₂ capture process have an inhibiting effect on ice crystal formation. It is not clear whether the potential inhibiting effect is due to the chain length of amines or due to their geometry. If inhibition depends on the chain length as suggested in Schnell and Vali (1974), amines chosen for the CO₂ capture process are not expected to inhibit ice crystal formation. Thus the impact of amines on the ice-processing mechanism of rain formation is not further investigated in this work.

5.3 Amount of rainwater

The capture of supercooled droplets by an ice-phase precipitation particle (hydrometer) is usually termed accretion. Rainfall production thus includes rain drops from collision/coalescence and by accretion. Here only rainfall from collision/coalescence of liquid droplets is considered. Spontaneous coalescence of cloud droplets to form rain drops is called autoconversion. Simple parameterisations of the autoconversion of condensed liquid water from cloud droplets into rain drops exist, for example the parameterisation given by Berry and Reinhardt (1973). The autoconversion AC (in s⁻¹) is dependent upon the mass mixing ratio of cloud water, q_c (g liquid water per g air), the initial cloud droplet number concentration (equals the CCN concentration), N_c (in cm⁻³), and the mass dispersion, ν_m , of the initial droplet distribution:

$$AC = \frac{[\rho_0 \cdot q_c]^2}{[0.2 \cdot \rho_0] + [2.4 \cdot 10^5 \cdot q_c \cdot \nu_m / N_c]}^{-1} \quad (11)$$

ρ_0 is the density of air (g cm⁻³). The formulation exhibits a roughly cubic dependence on the cloud water mixing ratio, a direct dependence on the initial

mass dispersion and an inverse dependence on the initial CCN number concentration. An increasing number of CCN will thus decrease the autoconversion rate since a cloud initially formed with a larger number of CCN has a longer lifetime. Using the parameters in Table 2, a mass mixing ratio of 0.003 g cloud water per g air, a droplet mass dispersion of 0.7 and air density at ground level standard pressure, the autoconversion is calculated for the plume cloud containing amines. Using the initial number concentration of CCN increases of 600 cm^{-3} at 0.1 ppbv MEA and 1380 cm^{-3} at 1.0 ppbv MEA at 0.1% super saturation, the resulting autoconversion rates are 7.3×10^{-12} and $3.2 \times 10^{-12} \text{ s}^{-1}$, respectively. Thus for the higher gas phase MEA concentration, the autoconversion is smaller. AC is roughly proportional to v_m/N_c at a fixed liquid water mixing ratio. However, it is not likely that v_m is the same for the two initial cloud droplet distributions. An increase of the CCN number concentration due to the higher amine concentration in the droplet will be accompanied with a broader mass dispersion of the initial cloud-drop spectrum. Yet the cloud droplet mass dispersion cannot be estimated in a simple way but has to be calculated with a dynamic aerosol/cloud model.

To calculate the net production rate of rain water falling to the ground (PR), the rate of evaporation of rain drops (ER) has to be subtracted from the rain production rate (AC) obtained by the autoconversion of cloud water:

$$PR = AC - ER \quad (12)$$

A vertical profile of the time-dependent rain water mixing ratio (mass rain water per mass air) can be calculated with simplified one-dimensional models, e.g. the model developed by Srivastava (1967). In this model the interactions between cloud dynamics and microphysics can be investigated. Ice-phase processes and turbulence are neglected and cloud water is assumed to convert spontaneously to rain water when the threshold cloud water content is exceeded.

6 Worst case scenario

The emission estimate described in chapter 2 can be seen as a worst case estimate and the estimated MEA atmospheric concentration of 13 ppbv in the CO₂ capture plant plume is probably an overestimate of the actual plume concentration, as the plume is diluted by entraining of fresh air with increasing distance from the plant. The Henry's Law constant of MEA is about 3 to 4 orders of magnitude higher than the Henry's Law constant for ordinary alkyl amines. That implies a much higher solubility of MEA and of other hydroxyl amines in droplet water. The influence of amines on the surface tension of aerosol droplets is estimated by using an approximation for the particle surface tension derived for dissolved organic carbon in ambient fog and cloud droplets. By using this empiric relation for amines, the calculated surface tension reduction was stronger than the surface tension reduction found in experiments that investigated amine solutions (e.g. Aguila-Hernández, 2001). Thus the change of the saturation ratio due to addition of amines was probably overestimated in this study. The saturation ratio curve c) in Figure 4 for a gas phase concentration of 10 ppbv MEA can thus be seen as a worst case. In this case, the total aerosol droplet population would become

activated at 99% relative humidity inside the plume. Given sufficient water vapour content, this situation leads to a rapid formation of a plume cloud containing dissolved amine. If rainfall from this cloud occurs in addition depends on the temperature, specific humidity and meteorological stability (convective raise of the air parcel) of the boundary layer.

7 Further improvements and recommendations

There are some remaining issues that should be elaborated in more detail to proceed with this study:

1. The mass transfer of a gas phase species through the air-water interface to the aerosol water droplet should be described by a kinetic approach instead of the gas phase/water equilibrium that was assumed in this work.
2. The effect of ionic strength has to be considered for highly concentrated solutions. It can be expected that initially dissolved amines are highly concentrated in the small droplets and therefore the droplet solution cannot be treated as an ideal solution. Activity factors for the species involved in the equilibrium reactions (dissociation of amines) should be applied to the aerosol water droplets.
3. To exactly determine the influence of dissolved amines on the surface tension of aerosol droplets, experimental data on surface tension of amine solutions with different concentrations of amines and different temperatures should be retrieved from literature and the Szyszkowski-Langmuir equation should be fitted to this data.
4. An aerosol model should be selected or developed that enables the treatment of droplet growth from submicron to millimetre sizes based on the Köhler equation and the subsequent production of rain drops. Two possible types of aerosol models can be used:
 - a) A sectional aerosol model that calculates the concentration of activated CCN and the cloud droplet size distribution can be used in combination with the autoconversion approach. The rain production is calculated assuming spontaneous conversion of cloud water into rain water.
 - b) A model that is able to simultaneously solve the size spectrum of dry aerosol mass (non-activated aerosol) and the size spectrum of aerosol water mass (water droplets). A detailed collision/coalescence kernel could be included to enable the calculation of the amount of rainfall.
5. Coupling of the microphysical aerosol/cloud model with a meteorological model that describes the transport of the aerosol droplets under certain meteorological conditions. The meteorological model can either be a simple air parcel model, a plume dispersion model or a one-dimensional column model.

With the equilibrium model approach outlined in Chapter 3 it is shown that emission of amines promote the formation of supercritical droplets that can cause rainfall from the plume. It could be shown that the saturation ratio over fine

droplets is very sensitive to expected concentrations of MEA in the plume (between 1 and 10 ppbv MEA). The presented approach has several limitations as described above. The approach describes an equilibrium situation for a given aerosol population and does not consider the temporal development of droplet growth. Amines enhance the probability that very small water droplets can grow to cloud droplet size (10-20 μm) and cause rain formation in the plume of the CO_2 capture plant.

It is recommended to continue research on effects of amines on rainfall from plume clouds of CO_2 capture facilities. In a next step a dynamic aerosol model should be developed to study the temporal evolution of droplets based on the Köhler equation. In addition experimental work in a fog chamber is proposed to evaluate the change of droplet characteristics through the addition of amines. Finally, to predict the possibility of rainfall and the amount of rain water for certain meteorological conditions the microphysical aerosol/cloud model should be coupled with a meteorological dispersion model.

8 References

- Aguila-Hernández, J., Trejo, A., Gracia-Fadrique. (2001) Surface tension of aqueous solutions of alkanolamines: single amines, blended amines and systems with nonionic surfactants. *Fluid Phase Equilib.*, *185*, 165-175.
- Berry, E.X., Reinhardt, R.L. (1973) Modelling of condensation and collection within clouds. Reno, University of Nevada (Technical report series: Physical Sciences Publication, No. 16).
- Birstein, S.J. (1960) Studies on the effect of chemisorbed impurities of various AgI aerosols. In: *Physics of Precipitation*. Ed. by: H. Weickmann. Washington, American Geophysical Union (Geophysical Monograph No. 5). pp. 247-251.
- Davis, C.I. and Steele, R.L. (1968) Performance characteristics of various artificial ice nuclei sources. *J. Appl. Meteor.*, *7*, 667-673.
- Facchini, M.C., Mircea, M., Fuzzi, S., Charlson, R.J. (1999) Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature*, *401*, 257-259.
- Fukuta, N. (1966) Experimental studies of organic ice nuclei. *J. Atmos. Sci.*, *23*, 191-196.
- Georgii, H.W. (1963) Investigations on the activation of inorganic and organic freezing-nuclei. *J. Appl. Math. Phys.*, *14*, 503-510.
- Sander, R. (1999) Compilation of Henry's Law constants for inorganic and organic species of potential importance in environmental chemistry, Version 3. URL: <http://www.henrys-law.org> [04.11.2008].
- Schnell, R. and Vali, G. (1974) Heterogeneous ice nucleation in the presence of aliphatic amines and ammonia. Wyoming Univ. (Report No. AS113).
- Srivastava, R.C. (1967) A study of the effect of precipitation on cumulus dynamics. *J. Atmos. Sci.*, *24*, 36-45.
- Tang, D. (1980) Deliquescence properties and particle size change of hygroscopic aerosols. In: *Generation of aerosols and facilities for exposure experiments*. Ed. by: Willeke, K. Ann Arbor, MI, Ann Arbor Science Publishers. pp. 153-167.
- Wise, M.E., Garland, R.M., Tolbert, M.A. (2004) Ice nucleation in internally mixed ammonium sulphate/dicarboxylic acid particles. *J. Geophys. Res.*, *109*, D19203, doi:10.1029/2003JD004313.

