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Effect of Amine Volatility on Aerosol Droplet Development in Absorption Columns

Hammad Majeed[a] Hanna Knuutila[a] Magne Hillestad[a] Hallvard F. Svendsen[a]*

[a]Norwegian University of Science and Technology, Trondheim 7491, Norway

Abstract

In absorption processes aerosols are generated by spontaneous condensation or desublimation processes in supersaturated gas phases. Amine volatility is a vital screening parameter for amines to be used in CO_2 capture. Higher volatility will result in higher losses through the gas phase and may also result in undesired aerosol formation and thereby to higher amine emissions and environmental impact. These amine emissions are one of the challenges in the realization of full scale absorption based post combustion CO_2 capture plants. It is crucial to understand the mechanisms governing in particular the aerosol formation and development through a column as this is not well understood.

Rigorous modelling of aerosol dynamics leads to a system of partial differential equations. In order to understand mechanics of a particle entering an absorber an implementation of a droplet model is created in Matlab. The model predicts the droplet size, the droplet internal variable profiles and the mass transfer fluxes as function of position in the absorber. The focus of this paper is to study the effect of amine volatility and how this influences the droplet composition, growth rate, final size and the resulting amine loss.

* Corresponding author. Tel.: +47-95141784
   E-mail address: hallvard.svendsen@ntnu.no

1. Introduction

Global climate is changing due to greenhouse gas emissions and carbon dioxide (CO_2) accounts for about 77 % of all greenhouse gases released to the atmosphere [1]. The main source of CO_2 emissions is from burning of fossil fuels. Fossil fuel today accounts for 80% of the total world energy demand [2] and their total use is unfortunately is not foreseen to decrease. Absorption into amine solvents is presently the most economical and technically mature retrofit process for post-combustion carbon dioxide (CO_2) capture from large power plants [3].

Spontaneous condensation or desublimation mechanisms in supersaturated gases create aerosols. Supersaturation of a gas phase is the precondition and the first step of aerosol formation. The undesired aerosol formation in gas–liquid contact devices such as in absorption processes is a well-known phenomenon in the industry since more than 60 years. It has been described and explained in various publications [4,5]. A comprehensive survey on aerosol formation in absorption or wet scrubbing processes is given by[6].

Since detailed experimental data do not exist, in order to understand the development and build-up of these aerosols a detailed simulation tool is required that is able to predict aerosol formation and development as function of operational and chemical characteristics. A basic simulation tool for the description of aerosol development in CO_2 absorption columns is already established and described briefly below. For more details see [7]. This model gives examples as to how various entering droplets grow or shrink through an absorber and how their composition changes with respect to position. The present work is based on this model.

There are a number of publications on VLE data of the binary MEA-H_2O system and the volatility of amine has been studied broadly [8–10]. It can be considered that the effect of amine volatility on aerosol emission has not been studied yet [11].

Current work is established on the consequence of varying amine volatility on aerosol droplets. It is believed that higher volatility results in higher amine losses from absorption columns in terms of emissions. In one of the research work it is reported that volatility of 7M MEA is around 31 ppm (~77mg/Nm3) at nominal lean loadings which is quite high as compared to that of the design specification of ~12mg/Nm3 in treated flue gas of PCCC plants [10,11]. Thus, characterization of aerosol droplets considering volatility of amine is one of the important factors in realization of full scale CO_2 capture plants.

1.1. Modelling

The dimensionless equations of continuity and thermal energy in spherical coordinates, considering only the radial direction can be written as [7];

$$\frac{\partial C_x}{\partial t} = \frac{D_x}{R^2}\left[\left(\frac{2}{\xi}\cdot\frac{\partial C_x}{\partial \xi}\right)+\frac{\partial^2 C_x}{\partial \xi^2}\right]+r_x \tag{1}$$

$$\frac{\partial T}{\partial t} = \frac{k}{\rho\cdot C_p\cdot R^2}\left[\left(\frac{2}{\xi}\cdot\frac{\partial T}{\partial \xi}\right)+\frac{\partial^2 T}{\partial \xi^2}\right]+\frac{r_x\cdot\Delta H}{\rho\cdot C_p} \tag{2}$$

Where C_x and D_x indicate concentration and diffusion of any component respectively. Here r_x characterizes reaction rate. Density and diffusivity have been assumed constant.

In equation (2) ρ, C_p and k indicate density, heat capacity and thermal conductivity. While T is temperature and ΔH is heat of absorption.

The growth of the droplet is rate of change in volume with respect to time[7];

$$\frac{dV}{dt} = \frac{N_x \cdot A}{\rho_x} \tag{3}$$

N_x denotes the mass flux of transferring component e.g. amine and water, ρ_x represents density and A surface area.

In typical PCCC plants the reactions that may occur during CO_2 absorption are; ionization of water, dissolution of CO_2, dissociation of carbonate ion, amine protonation and carbamate formation depending on amine used.
In this work the kinetics of CO_2 and MEA solution is based on the termolecular or direct mechanism in which amine reacts with one molecule of a base and one molecule of CO_2 at the same time [12,13].
The concentration based rate equation for the carbamate formation reaction is given as:

$$r_{CO_2} = \left\{ K_{MEA}^T [MEA] + K_{H_2O}^T [H_2O] \right\} [MEA][CO_2] - \left(\frac{K_f^T}{K_{eq}^T} \right) [MEAH^+][MEACOO^-] \tag{4}$$

Where k shows kinetic rate constant i.e. of MEA and water, while K_{eq} & K_f is equilibrium kinetic rate constant and rate constant for the forward rate of reaction. The kinetic constants are defined with Arrhenius type temperature dependency and the equilibrium reaction constant is expressed in terms of activities[14].

2. Results

The model considers that the droplet follows the gas phase from bottom to top of the column with a velocity relative to the gas phase given by the droplet terminal velocity. This velocity is very small for typical aerosol droplets, see [7]. Six different cases are modelled as presented in Table 1 with varying MEA volatility and initial concentration to understand the behaviour of the droplet inside the column under different volatility conditions.

Table 1: Modelled Cases

Case 1	Droplet, initial radius 1.5μ, containing 0.0001M MEA travelling from bottom to top of column. Base case conditions.
Case 2	Droplet, initial radius 1.5μ, containing 0.0001M MEA travelling from bottom to top of column with increased volatility of amine by a factor of 10
Case 3	Droplet, initial radius 1.5μ, containing 0.0001M MEA travelling from bottom to top of column with decreased volatility of amine by a factor of 10
Case 4	Droplet, initial radius 1.5μ, containing 5M MEA travelling from bottom to top of column. Base case conditions.
Case 5	Droplet, initial radius 1.5μ, containing 5M MEA travelling from bottom to top of column with increased volatility of amine by a factor of 10
Case 6	Droplet, initial radius 1.5μ, containing 5M MEA travelling from bottom to top of column with decreased volatility of amine by a factor of 10

Base case conditions mean volatility of MEA according to e-NRTL model. As basis for the droplet behaviour, the absorber column gas phase composition and temperature profiles are needed. For this purpose an ASPEN simulation was performed using e-NRTL Rate Based MEA model [15]. The gas phase data was used in the 6 cases apart from the MEA partial pressures which were increased and decreased by a factor of 10 as for the volatility in the droplet.

2.1. Mass Transfer:

Before discussing results it is important to mention that there is only one dimensionless variable in this model and that is droplet radius. '0' on x axis indicates centre of droplet while '1' shows interface between droplet and surrounding gas phase.

In case 1 the droplet with initial size of 1.5 micron having a very low initial MEA concentration (0.0001 mol/L) is exposed to an atmosphere with changing gas phase composition. This case is modelled with actual conditions in which none of the equilibrium model parameters are altered, i.e. volatility. As the initial MEA concentration is low, MEA starts to diffuse into droplet from the surrounding gas phase and its concentration increases with the passage time through the column as depicted in Figure 1a. The carbamate concentrations also increase with position in the column because of diffusion and reaction of CO_2. It is however seen that the carbamate concentration goes through a maximum at about 11-12m and decreases toward the absorber top. The reason for this is the reduced CO_2 partial pressure in the top section of the tower. CO_2 starts rapidly to build up at the interface, but as MEA starts building up inside the droplet the reaction starts and the concentration of free CO_2 drops inside the droplet as it moves up in the tower. Initially, at the tower bottom, a concentration profile inside the droplet is visible but vanishes as it moves upwards because of the reaction with MEA.
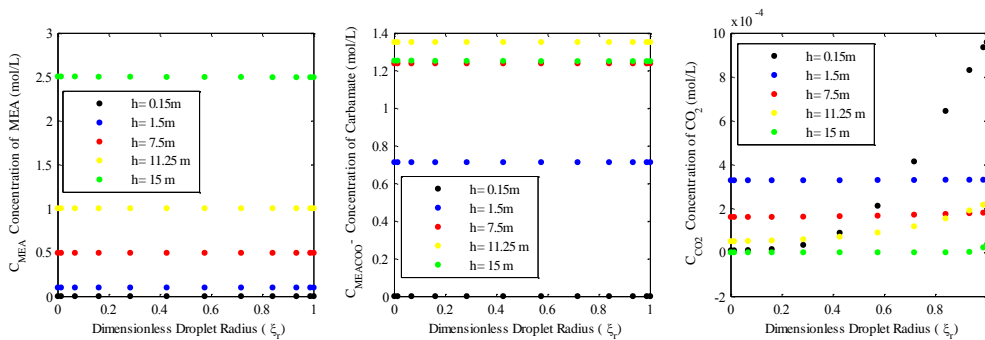

Figure 1 Case 1: (a) MEA Concentration profile, (b) Carbamate Concentration profile, (c) CO_2 Concentration profile

In case 2, shown in Figure 2, the volatility of amine is altered. In this case the partial pressure of MEA in the absorber gas phase and the equilibrium partial pressure of MEA over the droplet were both increased by a factor of 10 in order to see the effect of increase amine volatility. Otherwise conditions are the same as in Case 1.
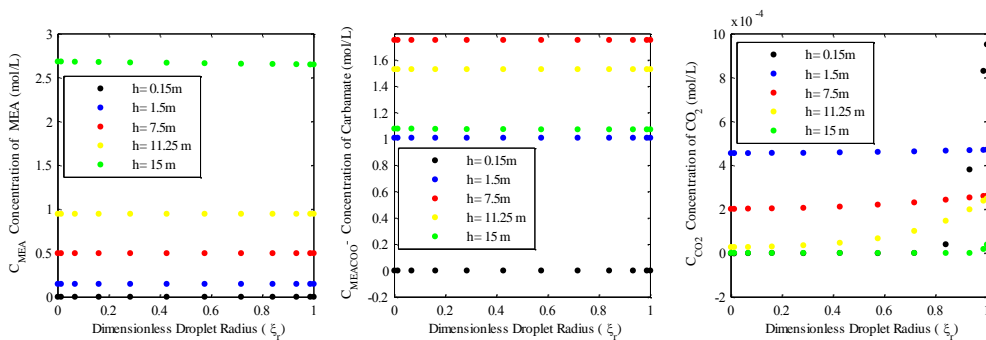

Figure 2 Case 2: (a) MEA Concentration profile, (b) Carbamate Concentration profile, (c) CO_2 Concentration profile

Comparing Figure 1a and 2a it is evident that MEA concentration builds up inside the droplet at about the same rate and that the final concentration is slightly higher than for the base case. The buildup of carbamate inside the droplet is higher than for Case 1 indicating that the more volatile solution has a tendency to take up more amine inside the

particle. Comparing Figures 1b and 2b it is also seen that carbamate forms faster in the high volatility case and reaches a maximum lower down in the tower. What may be somewhat surprising is that the effects are not stronger than seen. This has to do with the simultaneous transport of water into the droplet. The water volatility is not changes but with a buildup of MEA, more water will also be absorbed and shows up in the droplet size, as shown later, but not so much in the concentration levels. The CO_2 profiles shown in Figure 2c are similar to those of Figure 1c but it is seen that the initial CO_2 profile has a higher gradient in the high volatility case. The reason for this is the more rapid initial buildup of MEA and the subsequent reaction. However, at position 1.5m into the tower it can be seen that the free CO_2 concentration is higher in the high volatility case than for the base case. The reason for this is found in the more rapid buildup of carbamate combined with still relatively low free MEA in the high volatility case. The chemical reactions are rapid and at this point almost equilibrium exists between free CO_2, free MEA and carbamate, resulting in a higher free CO_2 concentration. Toward the top of the column the ratio between carbamate and free MEA moves in the favour of free MEA, thereby shifting the equilibrium toward less free CO_2 as seen both in Figure 1c and 2c. At the top the free amine concentration is so high that the free CO_2 concentration is very low.

In Case 3 the partial pressure of MEA in the gas phase and the equilibrium partial pressure are decreased by a factor of 10. All other factors are same as in the previous two cases. The free MEA concentration, Figure 3a, is seen to build up inside the droplet at a much lower rate as the two other cases and finally end up at a lower level than for the other cases, but still at about 2mol/L. This shows that an industrial column is capable of reaching close to equilibrium even for low volatility solvents, thus building up significant concentrations also in this case. This is somewhat contrary to common perception, but is reasonable. With any volatility equilibrium will predict about the same concentration levels in the droplet as in the main absorbent. What we have shown is that with industrial size columns and subsequent retention times, close to equilibrium is achieved even with very low volatility. However, lower down in the column, lower free MEA levels are found compared to Case 1 and 2. This naturally leads to lower concentration levels of carbamate as well. A striking difference is seen when comparing Figures 1c and 2c to 3c. In Figure 3c the initial CO_2 gradient is almost flat indicating that the diffusion of CO_2 is rapid compared to the combined transport of MEA and reaction.
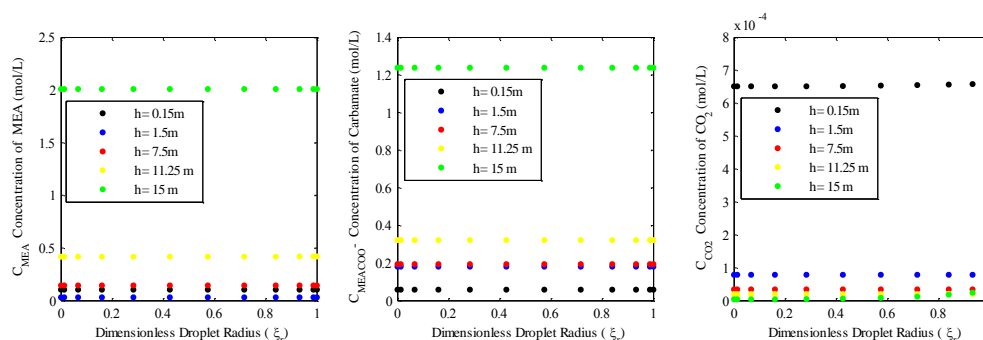

Figure 3 Case 3: (a) MEA Concentration profile, (b) Carbamate Concentration profile, (c) CO_2 Concentration profile

Cases 4-6 are similar to the previous cases, only the initial droplet MEA concentration is changed from 0.0001mol/L to 5mol/L.
In case 4 a droplet with initial radius of 1.5μ containing 5M MEA exposed to an atmosphere with changing gas phase composition and with base case volatility. The MEA concentration profiles are presented in Figure 4a, depicting that the droplet MEA concentration decreases gradually and actually goes through a minimum about half way through the absorber. Thereafter it increases again and ends up at close to the same level as shown in Figure 1a. Actually, already at 7.5m the free MEA concentration is close to the same as in Case 1.

This is reasonable as the surrounding gas phase is the same as in Case 1 and again this shows that the transport processes are fast enough in this case to erase differences in initial droplet concentration about half way up the tower. One should bear in mind that the droplet mass is so small that it has no influence on the surrounding gas.
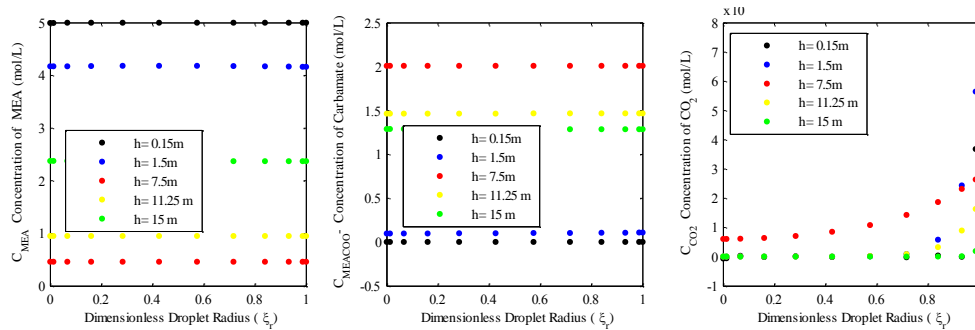
Figure 4 Case 4: (a) MEA Concentration profile, (b) Carbamate Concentration profile, (c) CO₂ Concentration profile

The development in carbamate concentration, given in Figure 4b can be explained in a similar way. The initial carbamate buildup is limited by the CO_2 mass transfer, as also shown by the steep initial CO_2 gradient in Figure 4c. The effect of the high initial MEA concentration is still visible at 7.5m where the carbamate concentration is significantly higher than shown in Figure 1b. Higher up in the column the situation is very similar to what is seen in Figure 1b. As mentioned the 5 mol/L initial concentration results in a very steep initial CO_2 profile. The gradient is still visible mid-way through the column indicating CO_2 mass transfer limitation at this point.

In case 5 the volatility of amine is increased by a factor of 10 and the free MEA concentration profiles are shown in figure 5a. Qualitatively Figure 5a shows the same as Figure 4a; the free MEA concentration starts at 5mol/L, goes through a minimum, and ends up very close what was found for initial MEA concentration 0.0001mol/L MEA in Figure 2a. However, the changes are more rapid than in Case 4. The minimum is found mid-way through the column and at the same free MEA level as for case 4, but already after 1.5m into the column, this level is nearly reached. The carbamate concentration goes through a maximum as also found in case 4, but the maximum is shifted up to between 7.5 and 11.25m into the column. The free CO_2 profiles are qualitatively similar in Cases 4 and 5, but generally the gradients are lower in Case 5. This mean that the CO_2 mass transfer limitation is more severe in Case 4 and this is the reason for the shift in carbamate maximum in Case 5. Toward the top of the column the concentration levels of all three components are very similar in Cases 5 and 2.
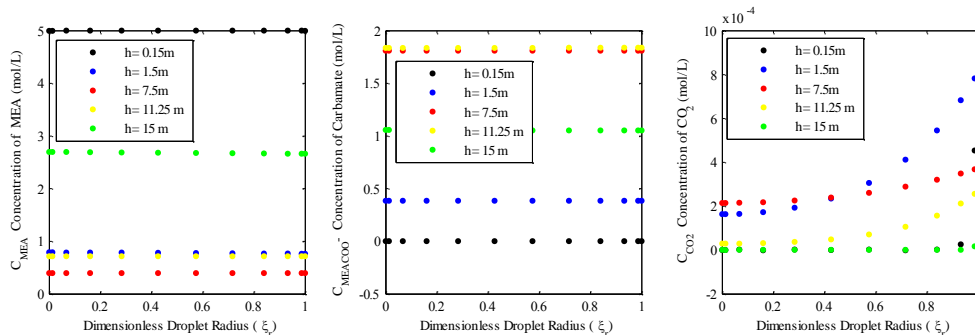

Figure 5 Case 5: (a) MEA Concentration profile, (b) Carbamate Concentration profile, (c) CO₂ Concentration profile

In Case 6 the partial pressure of MEA in gas phase and equilibrium partial pressure are decreased by a factor of 10 and the results obtained are presented in Figure 6.
When considering the free MEA concentration qualitative change is noticeable from what the higher volatilities gave. One may have expected that the free MEA after 1.5m should be higher than for Case 4. However, for Case 4 after 1.5m the free MEA concentration is about 4.2 mol/L whereas it has fallen to about 2 mol/L for Case 6. The reason for this may be the competition between MEA reacting with CO_2 inside the droplet and the transfer to and

from the surrounding gas. If the mass transfer is slow, in particular compared to that of CO_2, then MEA will react with CO_2 inside the droplet without rapidly being replenished from the surrounding gas. This happens in the low volatility case leading to a low MEA concentration after 1.5m as also shown in the much larger amount of carbamate formed at 1.5m in Case 6 compared to Case 4. The minimum in MEA shows up at 7.5m as also for Cases 4 and 5. The final concentrations for Case 6 for both MEA and carbamate are seen not reach the levels of Case 3. Thus in this case the MEA mass transfer rates are so low that the retention time in the absorber is not high enough for this to happen.
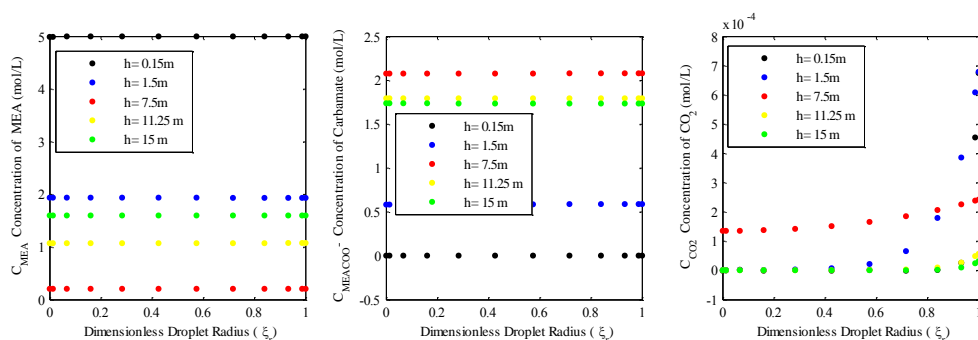

Figure 6 Case 6: (a) MEA Concentration profile, (b) Carbamate Concentration profile, (c) CO_2 Concentration profile

When comparing Figure 6c with 3c we see that starting with 5mol/L MEA creates limitations on the availability of CO_2 compared to MEA and initially this is rate limiting. However, toward the absorber top the CO_2 concentration gradients in Figure 6c are seen to be lower than for Cases 4 and 5 indicating that the mass transfer of MEA takes over.

2.2. Droplet Size

Maybe the most important factor related aerosol development is the growth of the droplet, whether it shrinks or grows in size by varying volatility. In Figure 7 the development in droplet size for cases 1-3 is shown. All droplets start out with 0.0001mol/L MEA. As is seen, in all three cases the start out by shrinking rapidly. The reason for this is that the water vapour pressure over the droplet is higher than in surrounding gas, so water evaporates. As water evaporates the MEA concentration inside increases because of concentrating up of the initial small amount of MEA, but mainly because of mass transfer of MEA to the droplet. As seen from the enlargement in Figure 7, after about 18-20 cm into the column, a level of MEA is reached where the water vapour pressure inside and outside are the same. Then because of further mass transfer of MEA to the droplet, also water starts condensing and entering the droplet. At first this is a slow process, in particular in the case of low MEA partial pressure, and thereby low mass transfer rate, Case 3. But, slowly MEA, carbamate and protonated MEA, build up and water has to follow, leading to an increase in the droplet size. As is seen the final size is very much dependent on the MEA "volatility". In the fictitious case with low volatility, Case 3, there is no increase in droplet size; on the contrary, the droplet shrinks. It should be kept in mind, however, that the total MEA concentrations (free, carbamate and protonated) in all cases are of the same order of magnitude. In the base case, Case 1, the final size is about 4.3 micron, whereas in Case 2 with 10 times the MEA volatility, the size only increased to about 6.3 micron. There thus seems to be a volatility, above which the growth in size slows down. One should of course keep in mind that the droplet volume is the third power of the radius.
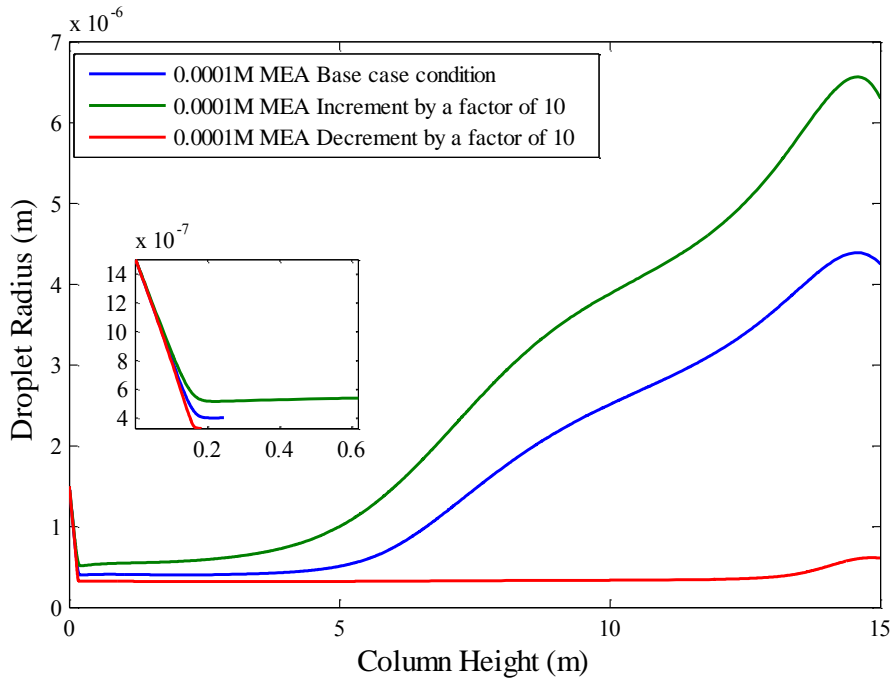
Figure 7: Droplet Radius (Case 1,2,3)

When the MEA concentration is increased to 5mol/L MEA the cases 4 to 6 are generated and shown in Figure 8.
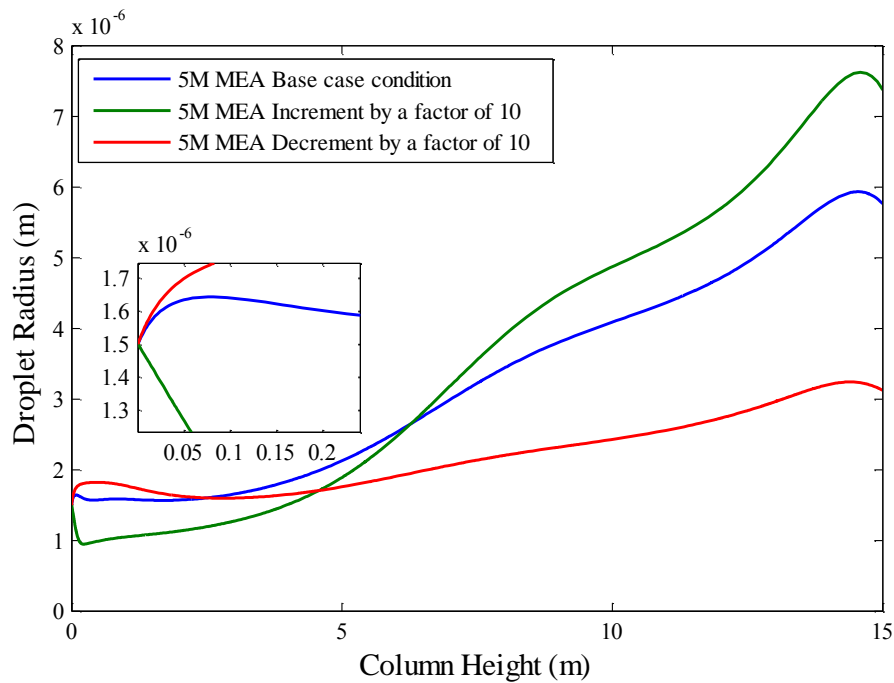

Figure 8: Droplet Radius (Case 4,5,6)

Change in initial behaviour can be seen in these cases. The surrounding gas composition is from an absorber simulation and since the bottom exit has rich amine as liquid phase, the MEA partial pressure above the droplet with fresh 5mol/L MEA will be higher than in the surrounding gas. There will thus be a driving for MEA evaporation.
On the other hand the water vapour pressure in the surrounding gas is higher than the equilibrium above the droplet entering. Thus water will tend to condense and MEA to evaporate. At low volatility of amine the water condensation dominates, leading to an initial increase in droplet size, gradually offset by increased MEA evaporation and a slowing down of water condensation. The opposite is seen with artificially high volatility, Case 3, where MEA evaporates faster that water condenses until a close to equilibrium is reached and the trend shifts as the surrounding gas composition also changes, and the droplet starts growing. For Case 1 which is the base MEA case both these initial tendencies are weaker and growth is seen almost throughout the absorber. It is seen that the final droplet size is larger for all cases with initial MEA concentration 5mol/L compared to the 0.0001mol/L ones. However, the differences are not dramatic.

2.3. Heat transfer

Mass transfer effects on internal variables profiles and size changes are discussed in the previous sections. In the model also sensible and latent heat transfer are taken into account. The surrounding gas temperature and partial pressures change throughout the absorber leading heat transfer, evaporation and condensation. The internal temperature profiles for all six cases modelled are shown in Figure 9. The figures show that there is a gradual increase in temperature through the column, partly because of transport of MEA, water and CO_2 in and out from the droplet including chemical reaction inside, but for the most part the temperature is dominated by sensible heat transfer from surrounding gas. This is seen by the profiles being relatively similar for all cases. What is not shown in these figures, due to lack of spatial resolution in the bottom part, is a rapid decrease in temperature cause by water or MEA evaporation.
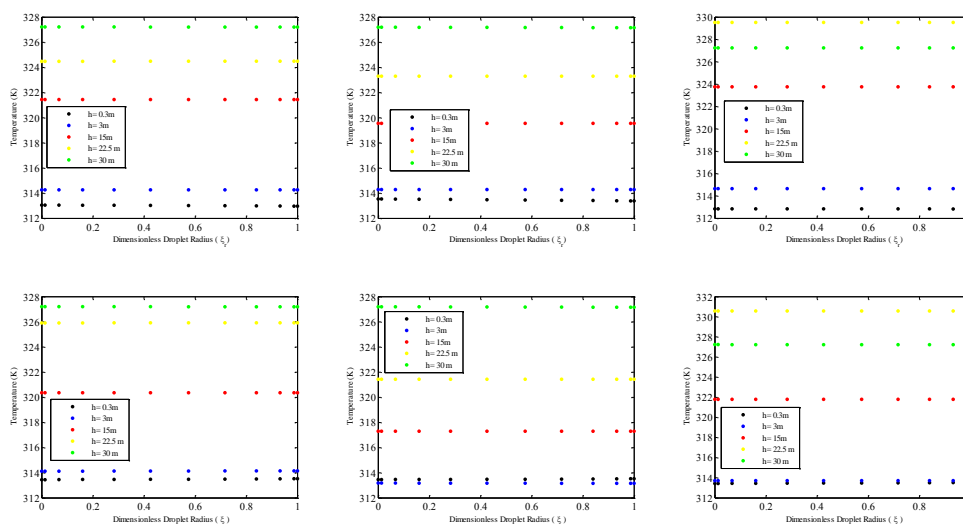

Figure 9: (a) Temp. profile (Case 1), (b) Temp. profile (Case 2), (c) Temp. profile (Case 3), (d) Temp. profile (Case 4), (e) Temp. profile (Case 5), (f) Temp. profile (Case 6)

The small differences seen are caused by the variation in MEA volatility. A tenfold increase in volatility hardly affects the droplet final temperature, Cases 1, 2, 4 and 5. When volatility is decreased by a factor 10 we see that evaporation and condensation hardly play any role and that the sensible heat transfer dominates. This is also in line with the small changes in droplet size seen for these cases.

3. Conclusions

Amine volatility is a fundamental screening criterion for amines to be used in CO_2 capture. Studies already published indicate that higher volatility results in higher amine losses from absorption columns in terms of emissions so the characterization of aerosol droplets considering amine volatility is one of the important factors in realization of full scale CO_2 capture plants. This study shows that a substantial increase or decrease in amine volatility does not alter dramatically the final droplet composition exiting the absorber, the reason being sufficient retention time in an industrial column for the mass transfer processes to proceed to about the same approach to equilibrium. This indicates that substantial amine losses through aerosols may be experienced even with low volatility solvents. A change of initial droplet composition, from 0.0001 to 5 mole MEA/L was similarly found not to dramatically change the final droplet composition. On the other hand, both volatility and initial composition affected final droplet size significantly: increased volatility led to larger droplet and vice versa. If droplets can be grown to sizes where impingement separation is possible, this may be a method of separation.

4. Acknowledgment

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