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Destruction of nitrosoamines with UV-light

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Abstract

In this paper the destruction of nitrosamines (NDMA and NDELA) in 30wt% MEA, 50wt% DEA and water wash solutions with UV-irradiation are presented and linked to measured penetration depths of UV-light. The results show that applying UV-irradiation in the solvent circulation loop would be challenging due to the very short penetration depths of UV-light into degraded/coloured amines solutions. However in water wash solutions the UV-light seems to effectively decompose the nitrosamines NDELA and NDMA.

1 Introduction

Global warming caused by anthropogenic CO_2 emissions is one of the most severe problems at present. Carbon Capture and Storage may offer a route to avoiding a major part of these emissions, and of the capture technologies, reactive absorption seems to be the most viable option to apply at this moment. However, in order to enable use of absorption processes on a global scale, one has to make certain that the processes are benign and do not create additional environmental problems. One of the issues that could be detrimental to the application of this technology is the formation and potential emissions of nitrosamines when using amines or amino acids as absorption reagents.

The formation of nitrosamines can be split into two sources: atmospheric formation from emissions of solvent amines from the plant and formation of nitrosamines in the process itself [1], [2],[3]. The exact formation rate of nitrosamines under normal operation is not known, but will be dependent on

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temperature, liquid phase composition and the oxygen and NO_x content of the gas phase. NO_2 is believed to be the critical component in NO_x and will dissolve in the liquid phase and may disproportionate into nitrate and nitrite.

In this paper the destruction of nitrosamines with UV-light is discussed and linked to measured penetration depths of UV-light. Results are shown for both fresh and degraded amines solutions. Some results for water wash sections are also presented.

Nomenclature

C   concentration of NDELA/NDMA at time t (ng/ml)

C_o Initial concentration of NDELA/NDMA before starting the UV-irradiation (ng/ml)

DEA   diethanolamine

LOQ   Limit of quantification

MEA   Monoethanolamine

NDELA N-Nitrosodiethanolamine

NDMA   N-nitrosodimethylamine

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2 Experimental work

To study the effect of UV-light under controlled conditions, a batch reactor system was used. The batch reactor system contained a 45L mixing tank, a centrifugal circulation pump, a valve to control the circulation rate, a commercial UV-light, a heating element located in the mixing tank and sampling points before and after the UV-light reactor. A schematic of the reactor system is shown in Figure 1. All the experiments were performed at room temperature. In the experiments a commercial Sterilight silver S8Q-PA UV-light reactor with lamp effect of 37W was used. All samples were withdrawn from the sampling point located after the UV-light reactor.
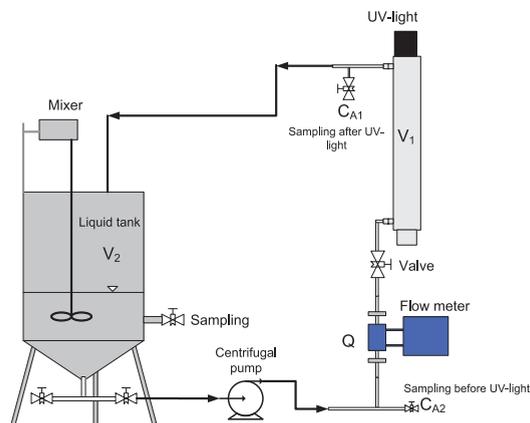

Fig. 1. **Batch reactor used in the experiments**

Experiments with fresh 30wt% MEA and artificial water wash solution were made. Additionally 30wt% MEA and 50wt% DEA solutions used in pilot campaigns were also tested. Some general information

about the campaigns is presented in table 1. The 30wt% MEA was used in 2 campaigns with total running time of 1690. The first campaign lasted for 700 hours during which the solvent was not exposed to O_2, NO or NO_2. During the second campaign, lasting 990 hours, the solvent was exposed to ~100 ppm of NO for 720 hours and to ~10oppm of NO_2 for 190 hours. Additionally, during the NO and NO_2 feed, oxygen was feed to the system so that oxygen concentrations from 5-10 vol% were reached. The DEA solution was used only in one 410 hours pilot campaign. During these, NO was fed to the system for 250 hours to give ~100ppm of NO. NO_2 feed was used for 100 hours. Towards the end of the campaigns 30wt% MEA and 50wt% DEA solutions were also exposed to 37 and 48 hours respectively of UV-light, respectively.

Table 1. General information

	30 wt% MEA		**50 wt% DEA**
Campaign	1	2	
Campaign duration	990 hours	700 hours	410 hours
NO feed (actual feeding hours) (~100ppm dry)	0 hours	720 hours	250 hours
NO_2 feed (actual feeding hours) (~10ppm dry)	0 hours	190 hours	100 hours
O2 feed (actual feeding hours) (5-10vol% dry)	0 hours	720 hours	250 hours
UV-light radiation in the main solvent circulation	0 hours	37 hours	48 hours

Penetration depths of the different solutions were measured by a UV-spectrophotometer (UV 2401 supplied by Shimadzu). The wavelength of interest was 254 nm. The cuvette used for measurement was washed three times with DI water followed by acetone wash and air drying after every measurement. After appropriate dilution, the sample was transferred to the cell. In the cell a beam of light passes through a 1 cm thickness of solution. A matching cell containing pure solvent was also prepared, and each cell was placed in the appropriate place in the spectrometer. After this two equal beams of ultraviolet light were passed, one through the sample solution and the other through the reference solvent. The intensities of the transmitted beams were then compared over the whole set wavelength range and the penetration depth was calculated.

NDELA and NDMA were analyzed using Liquid Chromatography-Mass spectrometry (LC-MS). The concentrations of MEA and DEA in the solutions were analyzed by titration and the CO_2 concentrations in the liquid phase were analyzed by the barium chloride method [4].

3 Results and discussion

3.1.1 Penetration depth measurements

The objectives of the penetration depth measurements were to find out how color and amine concentration affect the penetration of UV-light. Three different sets of experiments were performed.

First, different concentrations of fresh MEA and DEA solutions were prepared and the penetration depths of these fresh amine solutions were measured to determine the effect of presence of amine in the solution. The results are presented in Fig. 2. From the Figure it can be seen that the penetration depth decreases with increasing amine concentration for both MEA and DEA. The penetration depth decreases relatively fast with increasing amine concentration, especially at low concentrations. E.g. already for 0.5wt% MEA solution the penetration depth is 12% lower than that of pure water, respectively 38 and 43cm. In the Figure the penetration depth of MEA is lower compared that

of DEA. However when DEA and MEA are compared on mole-basis the penetration depths are very close to each other.
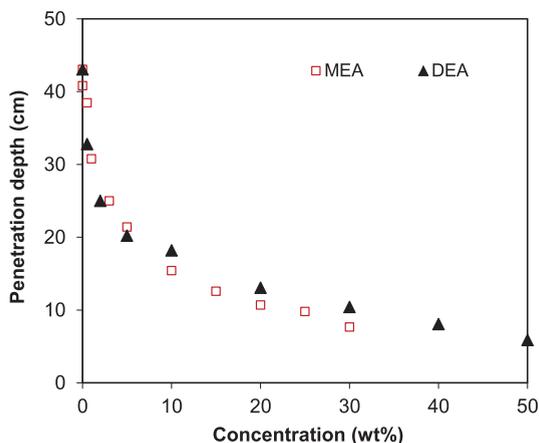

Fig. 2. Penetration depth as a function of amine concentration (fresh solutions).

Second, 30wt% MEA and 50 wt% DEA previously used in pilot campaigns, presented in short in Table 1, were mixed with fresh 30wt% MEA and 50wt% DEA solutions respectively in different ratios. The solutions from the pilot plant, taken out after the campaigns were done, were degraded and coloured whereas the fresh amine solutions were without colour. For this reason mixing these solutions would give solutions with constant amine concentration (either 30wt% MEA or 50wt% DEA) but with changing colour. The results are shown in Fig. 3a. From the figure it can be seen that as the fraction of pilot solution increases the penetration depth decreases rapidly. In other words, with increasing color of solution the penetration depth decreases. While fresh 30wt% MEA solution has a penetration depth of 7.7 cm, mixing this with 10% of used 30wt% MEA solution from the pilot decreases the penetration depth to 0.6 cm. A similar behavior is seen with the 50wt% DEA solution, even though the decrease is not as large. The pilot campaigns for DEA and MEA solutions were of different length and the color of the MEA solution was stronger compared to the 50wt% DEA solution. For that reason 30wt% MEA and 50wt% DEA should not be compared to each other, but Fig.3 should be merely used to conclude that color of the amine solution has a strong effect on the penetration depth.

Finally, to study the effect of a combined change of color and amine concentration, 30wt% MEA and 50 wt% DEA samples from the pilot were mixed with DI water in different ratios. In Fig. 3b the results are shown. From the results one can see that even with low amine concentrations (0.1 weight fraction of 30wt% MEA /50wt% DEA) the penetration depths are only 0.3 cm and 2.3cm for the MEA and DEA solutions respectively. These results indicate that the color of the solutions has a dominating effect on the penetration depth. Additionally it indicates that using UV-light to control the nitrosamine concentration would be difficult in any amine solution with color, even if the amine concentration were low.
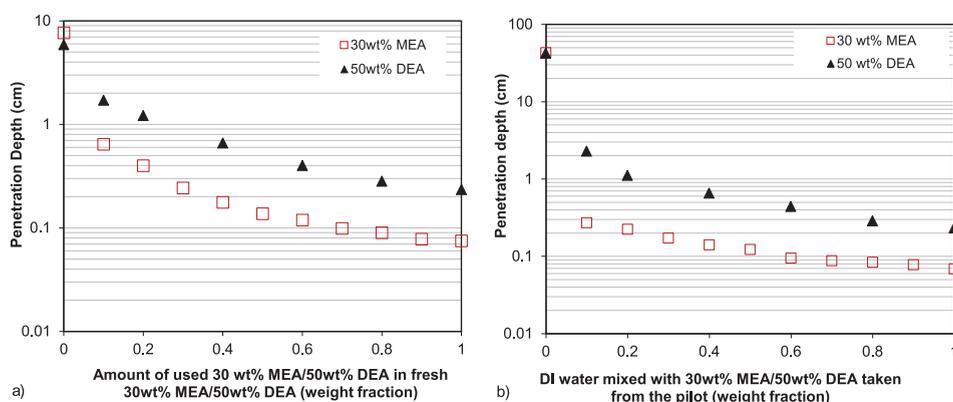
Fig. 3. (a) Penetration depth of 30wt% MEA and 50wt% DEA solutions taken out from the pilot after the campaign in fresh 30wt% and 50wt% DEA solutions, respectively. The 0 weight fraction solution is fresh 30wt% MEA/50wt% DEA and the 1 is the solution (30wt% MEA or 50wt% DEA) taken from the pilot plant after the pilot campaigns without any fresh amine solution. (b) Penetration depth of 30wt% MEA and 50wt% DEA solutions taken out from the pilot after the campaigns in DI water. The 0 weight fraction solution is pure DI water and the weight fraction 1 is solution taken out from the pilot plant after the campaigns.

Table 2. Composition of the artificial water wash solution. Based on LC-MS analysis except for NH_3, which is analysed with IC.

Component	Amount	Unit	Component	Amount	Unit
NH3	15.2	ng/ml	AMP	1.1	mg/ml
Dimethylamine	695	ng/ml	PZ	1.1	mg/ml
Methylamine	415	ng/ml	MEA	17.6	mg/ml
Ethylamine	380	ng/ml	NDELA	301	ng/ml
Diethylamine	569	ng/ml	NDMA	293	ng/ml

The amount of solution together with the start concentrations of NDMA and NDELA are shown in Table 3. From the results, shown in Fig. 4a it can be seen that the concentration of NDMA and NDELA are below the limit of quantification (LOQ) after 60 minutes. Additionally the semi-logarithmic relationship between the concentration and time implies that the reduction of nitrosamine by UV-light follows a first order kinetics in nitrosamine concentration. This finding is in a good agreement with literature where authors have reported that destruction of nitrosoamine follows 1st order kinetics with respect to nitrosoamine concentration [5], [6]. It is also clear that the rate of decay for NDMA is lower than that of NDELA. This was expected since in the literature the destruction kinetics has been reported to be dependent on the nitrosamine [5], [7].

Table 3. Overview of the experiments.

Experiment	Start concentration of NDELA (ng/ml)	Start concentration of NDMA (ng/ml)	LOQ NDELA (ng/ml)	LOQ NDMA (ng/ml)	Total amount of solution (kg)
Artificial water wash solution	290	307	5	25	29.4
Fresh 30wt% MEA	624		50		32.4
Fresh 30wt% MEA		7 620		250	29.9
Degraded 30wt% MEA	248		50		31.5
Degraded 50wt% DEA (1)	20 065		50		31
Degraded 50wt% DEA (2)	5 500		50		32

In Figure 4b results for a fresh, unloaded 30 wt% MEA solution spiked with NDELA and NDMA are shown. Here again, it is seen that the destruction follows first order kinetics. It can be seen, that the destruction rate of NDELA and NDMA are faster in artificial water wash solution compared to in 30wt% MEA. Modelling of the setup using first order kinetics with respect to the nitrosamine concentration shows that the kinetic constants of both NDMA and NDELA are reduced by a factor 3 when going from artificial water wash solution to fresh 30wt% MEA [8]. The difference seen in the destruction rate seems to correlate well with the penetration depth as for pure water the penetration depth is around 43cm as shown in Fig.3, whereas for fresh 30 wt% MEA solution it is 7.7cm and taking into account that the artificial wash water solution presented in Table 2 contains 20 g/L (2 wt%) of the main amines (AMP, PZ and MEA). If we assume that this amine mixture would have the same penetration depth as 2wt% MEA solution, it has a penetration depth of 28cm. The ratio between the penetration depths of 30wt% MEA and 2wt% MEA solution is 0.28, which is close to the change found in the kinetic constants for these solutions (1/3).
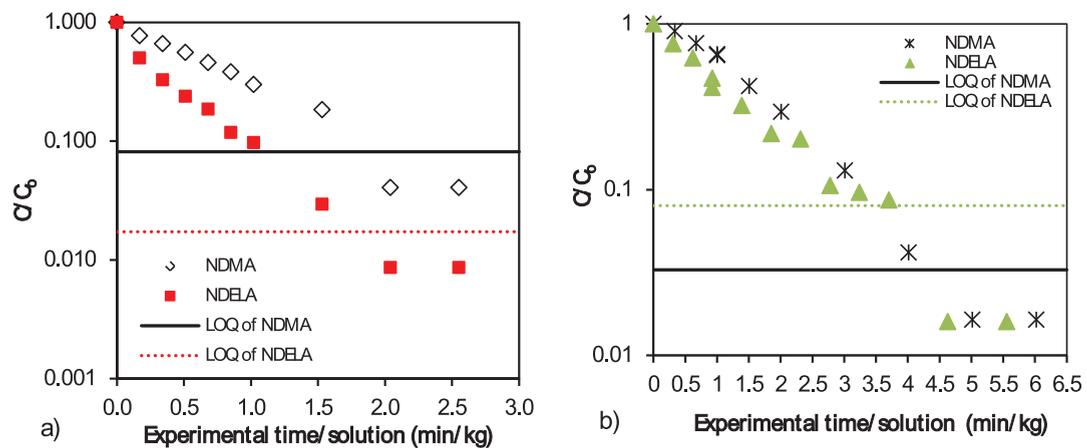

Fig.4.a) Decomposition of NDELA and NDMA in artificial water wash solution. b) Decomposition of NDELA and NDMA in fresh 30wt% MEA solution. All samples withdrawn after UV-light reactor. Sample withdrawn at 0min is taken before UV-light was tunred on.

3.3 Effect of UV-light in degraded solutions

The degraded 30wt% MEA solution from the pilot campaign (see Table 1) was also tested in the batch reactor system shown in Fig.1. The results, presented in Fig.5, clearly show that the decomposition of NDELA in degraded 30wt% MEA and in degraded 50wt% DEA is very slow. In fresh 30wt% MEA the NDELA was degraded from 620 ng/ml to 54 ng/ml (LOQ was 50 ng/ml) in 2 hours. However in the degraded 30wt% MEA solution from the pilot the time needed to decrease from 248 ng/ml to 70 ng/ml was 72 hours. 50wt% degraded DEA solution, previously used in the pilot, showed similar results. The degradation of NDELA is very slow requiring 72 hours to decrease from 5500 ng/ml to 330 ng/ml. As seen from the figure the decomposition of NDELA in 50wt% DEA is faster than in 30wt% MEA but still very slow.

Looking at the penetration depth measurements presented in Fig.3 we can see that the penetration depth in 30wt% MEA solution used in the pilot campaigns is 0.1cm whereas for a fresh 30wt% MEA it is 7.7cm. The ratio between the penetration depths is 77. From fig 4, we can see that to decay 50% of the NDELA present in 30wt% MEA we needed 0.75 minutes/kg solution. In case of the degraded 30wt% MEA presented in Fig.7 the time/kg solution needed to decay 50% of NDELA was 51 min/kg giving ratio of 69, which is close to 77. Even though this is a very simple way of illustrating the connection between the penetration depth and colouring of the solution, the penetration depth can be considered to give a good indication as to whether UV-light will be effective or not. The values presented here are not necessary generally valid for all UV-reactors. For example decreasing the liquid film thickness in the UV-reactor to 0.1cm would probably increase significantly the decomposition of degraded 30wt% MEA during the experiments.
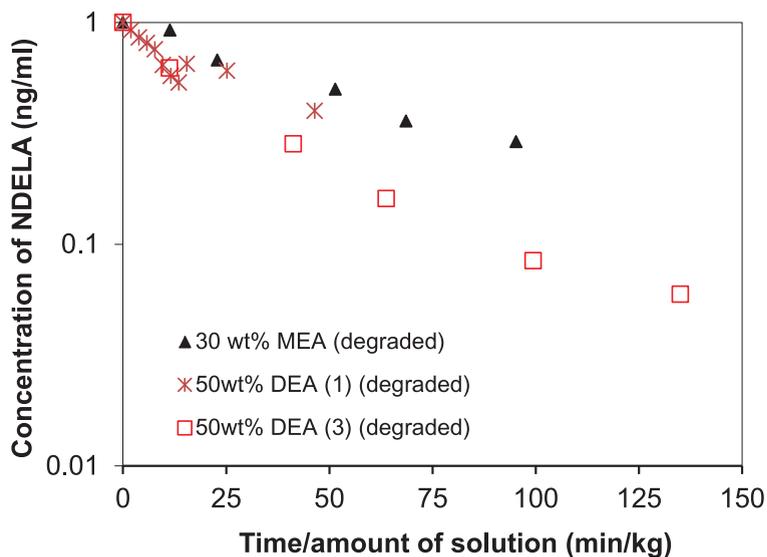

Fig. 5. Results for 30wt% MEA and 50wt% DEA solutions, which have been used in pilot plant.

In Fig. 5 two experiments with degraded 50wt% DEA solution are also presented and they agree very well until time 25 min/kg, where an unexpected increase in the analysed NDELA was noticed. The reason for this is not known. However, the decomposition rate in 50wt% DEA solution seems to be somewhat higher compared to the MEA result in Fig. 7. The penetration depth of the 50wt% DEA solution is 0.2cm as can be seen from Fig. 3. Also visually it was clear that the degraded 50wt% DEA solution had less color compared to the degraded 30wt% MEA solution. The difference in penetration depth and the high NDELA concentration in the DEA solution can explain the difference in the decomposition rate.

4 Conclusions

In this paper the feasibility of UV-light for decomposing NDELA and NDMA in amine solutions was studied and UV-light penetration depths into amine solutions were measured. The results clearly show that the decomposition is heavily affected by the colour of the solution. Also increased amine concentration leads to a decrease in decay of nitrosamines during UV-irradiation. The rate of decay of NDMA and NDELA was found to be different, NDELA decomposing faster than NDMA. The results indicate the UV-light could be used to decompose nitrosamines in water wash sections, but the effect of UV-irradiation in the main solvent loop would be small and the decay of NDELA very slow.

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