



Predicting supersaturation by rate-based simulations of reactive absorption



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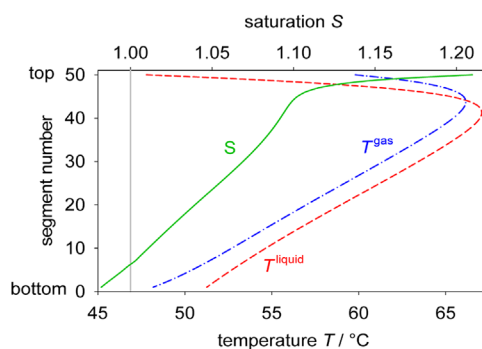
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HIGHLIGHTS

- Extended rate-based model for predicting supersaturation in absorption columns.
- Heterogeneous condensation in PCC absorption columns due to supersaturation.
- Detailed study of influence of various process parameters on the supersaturation.
- Estimation of solvent loss due to aerosol formation.
- Supports the development of countermeasures that prevent the formation of aerosols.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 February 2014

Received in revised form

10 July 2014

Accepted 14 July 2014

Available online 21 July 2014

Keywords:

Supersaturation
Absorption
Rate-based model
Amine
Carbon dioxide
Nucleation

ABSTRACT

A method for predicting supersaturation of the gas phase in absorption columns with rate-based simulations is presented. The method is used for studying reactive absorption of carbon dioxide in an aqueous solution of monoethanolamine (MEA). Supersaturation drives the formation of aerosols in absorption columns, which is important for solvent losses. The influence of different input parameters such as temperature of rich gas and solvent, and concentration of carbon dioxide in the rich gas on the supersaturation is studied. Saturation profiles in the absorption column are reported, and it is shown that the predicted saturation is in the range which is relevant for heterogeneous nucleation. The observed trends are in excellent agreement with the trends found for the aerosol formation in a carbon dioxide absorption column, which were recently reported in the literature. The approach presented here opens a route for modeling aerosol formation in absorption columns using rate-based models.

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1. Introduction

Supersaturation of the gas phase has been observed in many industrial absorption processes especially if strong acid components

like hydrochloric acid, bromic acid, or sulfuric acid are absorbed in aqueous solutions (Schaber, 1995). Caused by simultaneous heat and mass transfer the concentration of the condensable components in the gas phase may exceed the corresponding concentration in vapor–liquid equilibrium (VLE) so that the gas phase is supersaturated. As a result of the supersaturation of the gas phase, aerosols may be formed, initiated by heterogeneous or homogeneous nucleation (Brachert et al., 2013; Schaber, 1995; Wix et al., 2010). The aerosols

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can leave the process via the gas outlet and cause an increased emission of solvent compared to the case without aerosol formation.

Both for ecological and economic reasons, the solvent losses via the gas outlet are undesirable. On these grounds typically washing sections are used in absorption processes. Khakharia et al. (2013a) and Mertens et al. (2014) reported that in an absorption column for the removal of CO₂ with aqueous solutions of amine the emission of amine increased drastically when sulfuric acid aerosols were introduced in the rich gas as nuclei. The concentration of monoethanolamine (MEA) in the lean gas was much higher than the concentration expected from the volatility of MEA. Sulfuric acid is present in the rich gas when sulfur containing fuel is used for the combustion (e.g. coal fired power plants) and a wet flue gas desulfurization is employed (Srivastava et al., 2004). Khakharia et al. (2013a) conclude that the emission of MEA is caused by aerosols that are formed in the gas phase due to supersaturation and nucleation or due to reaction of CO₂ with MEA in the aerosol phase.

Commonly, reactive absorption processes are described with rate-based models. While equilibrium stage models are typically sufficient to describe (reactive) distillation (von Harbou et al., 2013; Pöpkén et al., 2001; Steinigeweg and Gmehling, 2002) they often fail for reactive absorption (Asprion, 2006; Kucka et al., 2003; Noeres et al., 2003). Wagner et al. (2013) recently presented a carefully validated physico-chemical model of the gas solubility of carbon dioxide in aqueous MEA solutions. That model was the basis for the development of the rate-based model for post combustion carbon capture (PCC) with aqueous MEA solution by von Harbou et al. (2014). As shown by von Harbou et al. (2014), this model predicts experimental plant data both in pilot and industrial plant scale well without any adjustment of parameters to the plant data.

In contrast to equilibrium stage models, in rate-based models the gas and liquid phase are only in equilibrium at the interface. The heat and mass transfer is explicitly accounted for and the bulk phases are generally not in phase equilibrium. Thus, rate-based models may be used for predictions of supersaturation of the gas phase. The supersaturation is the key property which determines both nucleation and droplet growth of aerosols. Detailed models which describe the aerosol formation based on calculations of the supersaturation have been developed e.g. by Schaber and co-workers (Brosig, 2009; Ehrig et al., 2002; Haep, 2000; Schaber, 1995; Wix et al., 2010). The systems which were investigated in these studies are either non-reacting systems or systems with strong electrolytes like HCl+water. An extension to complex reacting systems like the one studied in the present work requires the determination of the supersaturation for which we provide a method. In future work that method will have to be coupled with models describing the nucleation and droplet growth as well as the feedback of these processes with the supersaturation. This is a major task, which however can be solved based on the experience that has been gained with simple systems, see above.

In a recent publication Fulk and Rochelle (2013) have presented a model for the growth of a single droplet passing through an absorption column. The studied absorption is that of CO₂ in an aqueous solution of piperazine. Partial pressures of CO₂+water+piperazine are taken from a simulation of an absorption column based on a model taken from the literature. The partial pressures of these components at the droplet surface are calculated from the saturation conditions and an empirical fluid property model different from the one that is used in the column simulation. As it is a single droplet, there is no feedback between the growth and the state of the gas phase in the column. Nucleation is not discussed by Fulk and Rochelle (2013).

Up to our knowledge the first (and only previous) work in which the supersaturation of the gas phase in an absorption

column was determined by a rate-based simulation was that of Vogt and Heidenreich (1999) who studied the absorption of air in water or solution of NaCl+water.

Up to now, commercial simulation tools are not able to predict supersaturation in the gas phase by default.

In this work, we present for the first time a method for calculating the saturation in the gas phase of reactive absorption columns by means of an extended rate-based model. Furthermore, this method enables a (worst-case) estimation of the mass flow of solvent that is lost via the gas outlet because of supersaturation and aerosol formation.

A systematic study of the saturation profiles of the gas phase is performed for the reactive absorption of CO₂ in aqueous solutions of MEA with the rate-based model developed by von Harbou et al. (2014). A comparison of the simulation results to the experimental results of Khakharia et al. (2013a), Mertens et al. (2012) and Moser et al. (2013) is carried out. It indicates that the influence of different input parameters such as the temperatures of the solvent or the rich gas, and the concentration of CO₂ in the rich gas on the saturation is well described by the model.

The method presented here is generic and can be applied to any solvent in absorption processes.

2. Saturation and nucleation

For defining the saturation S of a gaseous mixture at a given temperature T and pressure p , its N components are classified as either condensable ($i=1, \dots, N_c$) or non-condensable ($i=N_c+1, \dots, N$). A component is considered to be condensable if it is found in the first droplet formed when the gas is compressed at constant temperature T . The mole numbers in the studied mixture are $\mathbf{n} = (n_1, \dots, n_N)$. After removing all non-condensable components, the so-called "mixture of condensable components" is obtained. The mole numbers in that mixture are $\mathbf{n}^* = (n_1, \dots, n_{N_c})$. From the mole numbers given for the two mixtures, mole fractions y_i and y_i^* can be calculated.

It is assumed that the studied gaseous mixture is a mixture of ideal gases. The saturation S of that mixture is defined as the sum of the partial pressures of all condensable components in the mixture divided by the dew point pressure p^{dew} of the corresponding mixture of the condensable components:

$$S(T, p, \mathbf{y}) = \frac{p \sum_{i=1}^{N_c} y_i}{p^{\text{dew}}(T, \mathbf{y}^*)} \quad (1)$$

The gas phase is supersaturated if $S > 1$. In the simulation of the absorption of CO₂ from rich gas with aqueous solution of MEA, the components MEA, water, carbon dioxide, nitrogen and oxygen are considered in the gas phase. Nitrogen and oxygen are considered as non-condensable; MEA, water and carbon dioxide as condensable. CO₂ reacts with the solvent and forms HCO₃⁻, CO₃²⁻, and MEACOO⁻ (the carbamate of MEA). These reactions are implicitly taken into account in the definition given above.

The formation of aerosols is caused by two different mechanisms: homogeneous or heterogeneous nucleation. For homogeneous nucleation, the necessary saturation is larger than 2–6 for water (VDI, 2010). The number for the saturation required for homogeneous nucleation of other substances with similar properties (e.g. surface tension) is in the same range as for water (Wix et al., 2007). Heterogeneous nucleation occurs if nuclei are present in the gas phase and the saturation exceeds a certain value known as the critical heterogeneous saturation $S_{\text{crit}}^{\text{het}}$. For a given mixture, the critical heterogeneous saturation is a function of the temperature, the wettability and the radius of the nuclei.

Studying pure fluids Thomson (1871) has obtained a relation between the saturation S of a gas phase surrounding a stable

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