Vapor-Liquid Equilibrium and Enthalpy of Absorption of the CO_2-MEA-H_2O System

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Amine scrubbing is widely used to remove acid gases, mainly CO_2 and H_2S, from various process gaseous streams, because of the enhancement due to chemical reactions occurring in the liquid phase.

For designing the acid gas removal plant, information on the heats of absorption of carbon dioxide in amine aqueous solutions is of paramount importance. Due to the exothermicity of reactions, a temperature increase occurs in the absorber, affecting the equilibrium and the amount of absorbed acid gas, while in the regenerator the energy requirement at the reboiler strongly depends on the heat of desorption.

This work is focused on the removal of CO_2, a powerful greenhouse gas, from flue gases by means of aqueous solutions of monoethanolamine (MEA), an industrial technology which is part of carbon capture and sequestration, to limit global warming.

The aim is the study of the CO_2-MEA-water system, in particular as for thermodynamics. The Electrolyte-NRTL model is used for the description of Vapor-Liquid Equilibrium as well as for the computation of the heat of absorption, considering the influence exerted by thermodynamic parameters.

The obtained parameters, checked against experimental data of VLE and of heat of absorption, can be implemented in the commercial software ASPEN Plus® and employed for simulations of the amine scrubbing scheme.

1. Introduction

In the last years, increasing attention is being paid to the problem of global warming, due to the presence of greenhouse gases produced by anthropogenic activities (Damartzis et al., 2013). In order to reduce the amount of these gases in the atmosphere, in particular of carbon dioxide, processes for removal have been developed (Neveux et al., 2013; Puccini et al., 2013). Industrially, absorption by means of alkanolamine solutions is often preferred to other removal systems and different studies can be found in literature (Kohl and Nielsen, 1997). Chemical absorption of carbon dioxide in aqueous solutions is controlled and enhanced by chemical reactions that take place in the liquid phase (Molina and Bouallou, 2013). Monoethanolamine is one of the most used amine in industrial acid gas removal, in particular when dealing with emissions from power generation. MEA is characterized by high reactivity, low solvent cost, low molecular weight, reasonable thermal stability and low thermal degradation rate (McCann et al., 2008). However, some fundamental disadvantages of MEA include the fact that loaded solutions are corrosive and that the enthalpy of reaction is high, causing a high energy requirement at the reboiler of the solvent regenerator. For this reason, regeneration is the most expensive section of the plant. Information on heats of absorption for acid gases in amine solutions is of prime importance for designing unit operations of acid gas removal, so a reliable prediction of this quantity is desirable. The aim of the work is obtaining a model which properly describes both the vapor-liquid equilibrium and the heat of absorption of the system composed of CO_2, MEA and water for several amine concentrations and for a wide range of temperatures and pressures, in order to use this tool to carry on the research in the reduction of the energy cost of this acid gas removal process.

In this work, a new regression of significant thermodynamic parameters has been performed, on the basis of available vapor-liquid equilibrium data. The obtained parameters have been used to evaluate the enthalpy of absorption of carbon dioxide. Results show that the method proposed in this paper allows a representation of both VLE and ΔH_{abs} in good agreement with the experimental evidence.

2. Thermodynamic framework

VLE in amine solvents has been thoroughly modeled in the past (Austgen et al., 1989; Freguia, 2002; Liu et al., 1999; Zhang et al., 2011), based on VLE measurements and data. However, not all the authors have considered the influence of VLE parameters on the representation of the enthalpy of absorption of carbon dioxide in the solvent. Indeed, while many data on gas solubility for wide ranges of temperature, pressure and amine concentration are available in literature (Jones et al., 1959; Jou et al., 1995; Lee et al., 1974; Lee et al., 1976; Ma'mun et al., 2005; Maddox et al., 1987; Shen and Li, 1992; Wagner et al., 2013), very few thermal data, taken from direct measurements, can be found, at 298 K (Arcis et al., 2011) and at higher temperatures (Carson et al., 2000; Mathonat et al., 1998).

From a thermodynamic point of view (Pellegrini et al., 2012), the system composed of CO_2, amine and H_2O is strongly non-ideal and needs to be properly represented (Langé et al., 2013; Moioli and Pellegrini, 2015b; Pellegrini et al., 2013): efforts to obtain a good description have been made firstly by Kent and Eisenberg (Kent and Eisenberg, 1976), who proposed a simplified model based on chemical reactions. Later, Chen and coworkers (Chen et al., 1979; Chen et al., 1982; Chen and Evans, 1986; Mock et al., 1986) developed a more rigorous model, taking into account the local composition of species, influenced by the presence of ions. Their model, Electolyte-NRTL, is widely used to model amine systems (Pellegrini et al., 2011) and has been taken as a basis for further developments, including the estimation of the vapor phase with different methods, as the PC-SAFT equation (Zhang et al., 2011).

Absorption of carbon dioxide in amine solutions is enhanced by chemical reactions in the liquid phase (Moioli and Pellegrini, 2015a; Moioli et al., 2013). In particular, when the solvent is an aqueous solution of MEA, the formation of a carbammate is involved (Moioli and Pellegrini, 2013). The set of chemical equilibrium reactions can be found in previous works on MEA scrubbing (Moioli et al., 2014). The same references report also the expression used for Henry's constant of carbon dioxide in water, while for vapor pressures of water and MEA the Extended Antoine equation (AspenTech, 2014) applies, with ASPEN Plus® default parameters.

The carbammate formation is associated with a high enthalpy of reaction (McCann et al., 2008), so reversing this reaction in the stripper requires large quantities of energy, making the process energy intensive. In the aqueous phase CO_2, MEA and H_2O reacts and, by dissociation or protonation, produce ions. The description of the VLE system, then, is complicated by the presence of dissociated species, which are not interested by migration to the vapor phase, that is usually described by means of an Equation of State. The Electrolyte-NRTL model takes into account the presence of ions: it describes the strongly non-ideality of the system by calculating the excess Gibbs free energy as a sum of several contributions, due to short-range interactions, mainly due to molecule-molecule and/or ion-molecule interactions, and long-range interactions among ionic species. The nature of the force can be different according to the strength of ion and the polarity of the molecule. Then, the excess Gibbs free energy is calculated as:

$$\frac{g^{Ex}}{RT} = \frac{g^{Ex}_{PDH}}{RT} + \frac{g^{Ex}_{Born}}{RT} + \frac{g^{Ex}_{NRTL}}{RT} \tag{1}$$

Long-range electrostatic interactions are the sum of Pitzer, Debye and Hückel contribution and Born ion-reference-state-transfer from infinite dilution in mixed solvent to infinite dilution in water (Austgen, 1989). The contribution of short range interactions is represented using NRTL theory (Renon and Prausnitz, 1968) based on the local composition of the system, considering the local composition around the single molecule different from the mean composition of liquid mixture. In particular, interactions are modeled assuming local electroneutrality and repulsion of ions of the same charge. The NRTL contribution is described as function of non-random parameters and binary interaction parameters (Eq.(2)) between components of the system. These parameters are temperature dependent and have to be calculated from experimental vapor-liquid equilibrium data. Interactions can be between two different molecules, a molecule and a couple of anion and cation or between couples of cations and anions and are not symmetric. Only binary interaction parameters are required for the description of complex systems.

Values of these parameters can be regressed from experimental data or found in literature. When the concentration of ionic species is high, ternary parameters may be required, but for systems of weak electrolytes binary parameters are enough to describe the system with good results.

$$\tau_{j,k} = A_{j,k} + \frac{B_{j,k}}{T} \neq \tau_{k,j} \quad j = \text{molec,ca,ac} \quad k = \text{molec,ca,ac} \tag{2}$$

The calculation of enthalpies derives from the calculation of activity coefficients, since the equation used for the electrolyte-NRTL enthalpy is (AspenTech, 2014):

$$H_m^* = x_w H_w^* + \sum_s x_s H_s^{*,l} + \sum_k x_k H_k^\infty + H_m^{*,E} \tag{3}$$

where H_w^* is the pure water molar enthalpy, calculated from the Ideal Gas model and the ASME Steam Table; $H_s^{*,l}$ is the enthalpy contribution from a non-water solvent, as MEA; H_k^∞ is the aqueous infinite enthalpy calculated for any ion or molecular solute; $H_m^{*,E}$ is the molar excess enthalpy, calculated from the activity coefficient model.

Moreover, Zhang et al. in 2011 showed in their work that the enthalpy of absorption is dominated by the heat generated by $MEAH^+$ ion and $MEACOO^-$ ion dissociation. The amount of the total heat released at chemical equilibrium is then strongly related to the amount of each species reacted or produced, which are influenced by the adopted thermodynamic model. A reliable thermodynamic tool, then, is needed not only for the description of the equilibrium between the vapor phase and the liquid one, but also for the determination of the amount of heat released by chemical reactions, and so the overall heat of absorption of carbon dioxide in the solvent.

3. Regression of VLE parameters

In the first part of this work regressions have been performed in order to find values for H2O-(MEAH+-MEACOO-), (MEAH+-MEACOO-)- H2O, H2O-(MEAH+-HCO3-), (MEAH+-HCO3-)- H2O adaptive parameter Aj,k and Bj,k for binary interaction parameters in the NRTL contribution to the liquid phase activity coefficient.

Experimental TPx VLE data have been taken from the work by Maddox et al. (1987), Shen and Li (1992), Lee et al. (1974) and Jou et al. (1995) and have been used to regress parameters with the Data Regression System in Aspen Plus®, using the Maximum Likelyhood method with the Britt-Luecke algorithm (Britt and Luecke, 1973).

Values for standard deviation on measured variables are set equal to Aspen Plus® default: 0.1 [K] for temperature, 0.1% for pressure, 0.1% for liquid phase composition, 1% for vapor phase composition. When data in literature are not completely reported (y_{MEA}), deviations of 100 % have been adopted for, taking into account the great uncertainty in the value of the calculated missing variable (Freguia, 2002).
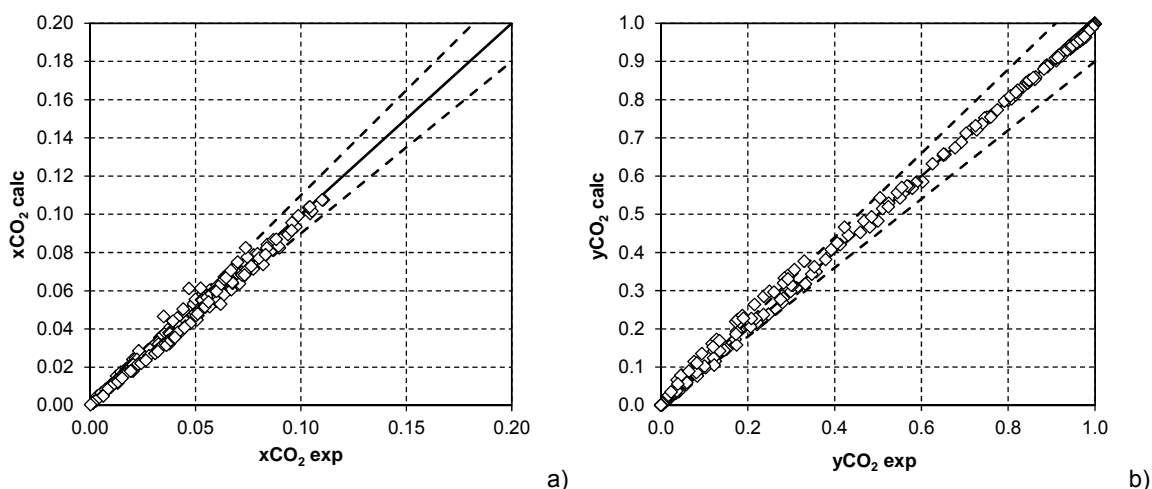

Figure 1: Parity plots of molar fraction of carbon dioxide a) in the liquid phase and b) in the vapor phase resulted by using the parameters obtained in this work

Results obtained from the model are checked against experimental data for carbon dioxide-water-MEA systems and compared with other Electrolyte-NRTL studies found in literature for the same system: Austgen (1989), Liu et al. (1999), Freguia (2002), Aspen Plus® (2010), Zhang and Chen (2011). While the first three works use the same approach used here, the fourth work is a bit different, since the authors (Zhang and Chen, 2011) use the PC-SAFT equation of state to the vapor phase properties. Parity plots with results obtained with the proposed parameters are shown in Figure 1. The reliability of the model is estimated using the average value percent of the absolute values of relative errors, calculated according to Eq. (4).

$$AAD\% = \sum_{1}^{NP} {}_i \frac{\left| z_{i,calc} - z_{i,\exp} \right|}{z_{i,\exp}} \cdot 100 \tag{4}$$

4. Model validation through heat of absorption

In literature very few works on direct measurements of enthalpy of absorption can be found (Arcis et al., 2011; Carson et al., 2000; Mathonat et al., 1998), since many other authors derive values from experimental results of VLE data and do not directly measure them by a flow calorimeter or other *ad hoc* instrumentations.

The commercial simulator ASPEN Plus® has been used as a tool for the evaluation of the enthalpy of absorption of carbon dioxide in the amine solution. All its default parameters can be changed according to the user's preferences and it is provided with the Electrolyte-NRTL.

A *Separator* unit with two feeds (a CO_2 stream and a solvent stream) and two outputs (a gas stream and a liquid stream) has been simulated, with the aim of best reproducing the experimental equipment used in the literature measurements. Temperature and pressure of the two fed streams and of the separation unit, as well as the molar flow rate and the composition of the CO_2 and the solvent stream are given as an input. Results are the amount of heat released during the operation, which consists in the heat of absorption of carbon dioxide in the solvent, and the characteristics of the streams coming out of the separation unit. From these results, the amount of carbon dioxide absorbed in the solvent and the heat of absorption per mole of amine or per mole of CO_2 can be calculated and compared to the experimental data.

Simulations with ASPEN Plus® default parameters, with literature models (Austgen, 1989; Freguia, 2002; Liu et al., 1999; Zhang et al., 2011) and with the proposed parameters have been performed and the obtained results have been compared to experimental values.

5. Results and discussion

Figure 2 shows a comparison of results with experimental data as parity plots. Being evaluated tests a lot, to better clarify results a detailed plot (for a range of loading usually found in industrial gas removal plants) has been added to the overall one, with the aim of allowing the reader to clearly compare the obtained results with the experimental evidence (Figure 3).
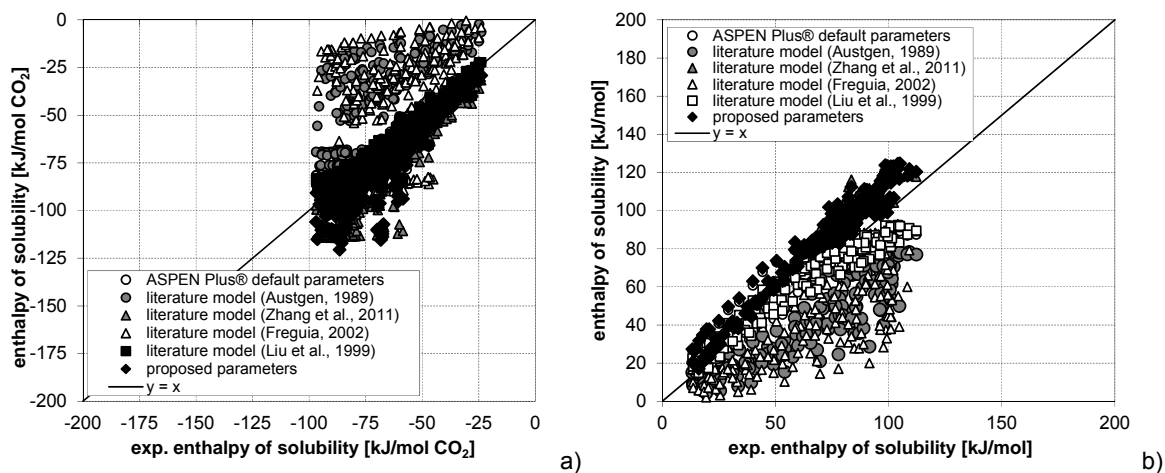

Figure 2: parity plot of results obtained with different methods of simulation of data by a) Mathonat et al. (1998) and b) Arcis et al.(2011)
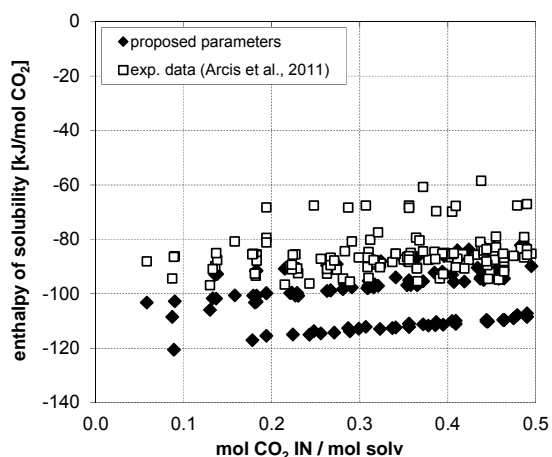
Figure 3: detailed results obtained with different methods of simulation of data by Mathonat et al. (1998) for loadings < 0.5.

The obtained parameters, regressed on the vapor-liquid equilibrium measurements, well reproduce the available experimental data of heat of absorption. The model could be further improved if a simultaneous regression of both VLE and ΔH_{abs} data could be performed, by using a tool external to ASPEN Plus®, which does not allow the user to consider ΔH_{abs} in the objective function of the regression.

6. Conclusions

Absorption by means of amine solution is widely industrially used to remove CO_2 to accomplish environmental regulations. Information on heats of absorption of CO_2 in amine solutions is of prime importance for designing unit operations because, due to the high enthalpy of reaction, the energy requirement at the reboiler of the regeneration section is high.

In this work a method able to describe both the VLE and the ΔH_{abs} of the CO_2-MEA-H_2O system has been used, based on thermodynamic parameters obtained by regression of experimental VLE data. The obtained results are considered in good agreement with the available literature data, allowing a reliable description of the absorption system.

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