



A consistent and transferable thermodynamic model to accurately describe CO₂ capture with monoethanolamine



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ABSTRACT

In this work, a consistent and transferable thermodynamic model to describe the carbon dioxide (CO₂) capture process with monoethanolamine (MEA) has been successfully developed within the framework of the soft-SAFT equation of state. The effect of the association interactions of the amine and alcohol groups contained in MEA have been isolated and characterized by studying the 1-alkylamines and 1-alkanols family. In a similar manner, the interaction between these functional groups and water has also been determined and later transferred to aqueous MEA. At the end, a reliable and consistent set of molecular parameters has been obtained for MEA. The CO₂ absorption process is described in terms of the aggregation of the reactants driven by the presence of strong intermolecular interactions. Descriptions of the density, vapor pressure and surface tension in these systems provide excellent agreement with the available experimental information. Also, a very good estimation of the CO₂ loading in MEA is found in the range of operating conditions. Predictions on the mixing enthalpies and the enthalpy of absorption are also given. This transferable model will allow the prediction of the CO₂ absorption process in other alkanolamines in the absence of experimental data.

1. Introduction

Carbon dioxide is very well known for its contribution to the greenhouse effect. Even if CO₂ is naturally present in the atmosphere, as a primary source of the Earth's carbon cycle, the effect of human action since the beginning of the industrial revolution in the last part of the XVIII century has caused a severe increase of its concentration. Currently, CO₂ levels in the atmosphere have drastically over passed the safety boundaries, causing a noticeable destabilization of the world-wide temperatures, the so-called global warming effect.

The main sources of human CO₂ emissions are due to industrial activities, coming from many different sectors, being the combustion of fossil fuels one of the major contributors [1]. Consequently, there is a need to capture this CO₂, separating it from the flue gas produced, in order to avoid its emission to the atmosphere. This is a primary concern and an essential step to later decide if CO₂ will be utilized as a raw material, such as in the carbonation of beverages, in supercritical CO₂ extraction processes or for Enhanced Oil Recovery (EOR) [2], or if it will be transported and stored in deep saline aquifers or in permeable and geologically stable underground layers.

Nowadays, there are several available possibilities on CO₂ capture,

depending on the type of industrial activity that is carried out [3,4]. In particular, there are three different lines related to the CO₂ combustion: pre-combustion capture, post-combustion capture and oxy-combustion capture [5,6]. The pre-combustion process consists on reacting a fuel with oxygen or air and/or steam to obtain a 'synthesis gas (syngas)' or 'fuel gas' composed mainly of carbon monoxide and hydrogen [7]. The second one is the most common and is carried out after the combustion. CO₂ capture in post-combustion processes can be done by chemical absorption [8], physical absorption [9], membranes [10,11] or adsorption [12–14]. Finally, the oxy-combustion consists on the use of oxygen instead of air for the combustion, obtaining a more purified CO₂ stream, easy to capture thanks to the low impurity levels [15].

Currently, the most popular method for post-combustion CO₂ capture is done by absorption in amines, where CO₂ flows from the bottom to the top of an absorption column, and gets in contact with an aqueous amine solution in counter current flow. Amines are usually regenerated in a desorption column, making the whole process highly efficient. However, this approach presents several drawbacks. The amines degrade at a relatively low temperature, particularly with the presence of oxygen in the flue gas [16], so low pressures are needed to minimize the degradation. This, in turn, lowers the capacity of absorption, since high

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Nomenclature

A^{res}	Residual Helmholtz energy
A^{ref}	Reference term of the Helmholtz energy
A^{chain}	Chain term of the Helmholtz energy
A^{assoc}	Association term of the Helmholtz energy
A^{polar}	Polar term of the Helmholtz energy
c	Influence parameter of surface tension
k_B	Boltzmann constant
ΔH	Enthalpy
LJ	Lennard-Jones
m	Number of LJ segments (chain length)

R	Universal constant of gases
T	Absolute temperature
T_c	Critical temperature
x_i	Mole fraction
α^{HB}	Binary parameter modifying the cross-association energy
ξ	Binary parameter modifying the cross-dispersive energy
η	Binary parameter modifying the cross-segment diameter
ε	Dispersive energy
ε^{HB}	Association site–site interaction energy
κ^{HB}	Association site–site bonding volume
σ	Segment diameter of the LJ monomer

solvent flow rates are required because of the low CO₂ partial pressure. In summary, between 0.35 and 2 kg of amines solution are consumed for every tonne of CO₂ captured, increasing the cost of the process due to solvent addition. Furthermore, the use of aqueous absorbents carries an energy penalty of about 30% of the energy produced in the plant [17]. Finally, special care should be taken with respect to equipment corrosion [16].

In spite of the abovementioned drawbacks of the amines chemisorption process, this is still the best technology available for capturing CO₂ at large scale. For this reason, this is the method employed in almost all carbon capture operation units around the world. However, there is still room for improvement, due to the variety of possible amines that can be used, as well as the particular considerations of the specific process from which CO₂ is going to be captured (purity of CO₂, amount of water, presence of other gases, etc.). In fact, the design and/or the optimization of a CO₂ capture process involves multicomponent mixtures where complex interactions occur. This, in turn, requires the use of accurate thermodynamic models that can reproduce the physicochemical behavior of a fluid, allowing the prediction of the different properties and phase equilibria of the pure compounds and mixtures involved at multiple thermodynamic conditions.

Traditionally, empirical correlations, activity coefficient models and cubic equations of state (EoSs) provided good results for some systems with a limited range of conditions and with few compounds. However, the precision they have in their range of actuation drops drastically if used out of that range, or if the system studied deviates from ideal behavior. In those situations, these approaches fail, providing inaccurate results. In order to overcome the limitations of classical equations and correlations, more complex models are needed. One possibility is to combine cubic EoSs with advanced mixing rules, such as shown in the contributions of Lasala and collaborators [18,19], applied to multicomponent systems involved in CO₂ capture processes. Another possibility is to use more fundamentally based equations that consider the molecular nature of the different compounds of the system. They are typically called molecular-based equations of state, developed from molecular modelling techniques and statistical mechanics concepts. The main advantage of the molecular-based equations in front of classical equations (such as Peng-Robinson, Soave-Redlich-Kwong, etc.) is the consideration of the different physical features of the molecule (chain, hydrogen-bonding, polarity, etc.) when building the theory. This is translated into a series of molecular parameters with physical meaning and independent of the fitting conditions. The parametrization of these molecular parameters is, however, a key step for the success of these approaches. When an adequate parametrization is carried out, the molecular base gives the equation predictive power and the ability to extrapolate the results [20]. The combination of a physical method with an engineering approach has been very successful to model the thermodynamic properties of complex systems, such as ionic liquids (ILs) [21–24], deep eutectic solvents (DESs) [25,26], or gas mixtures related to the Carbon Capture and Sequestration (CCS) technology [27]. In all cases, these equations provide a high degree of predictability and

extrapolation capability. In particular, the Statistical Association Fluid Theory (SAFT) [28,29], and its subsequent improvements, have become the most well-known and successful tools for this purpose.

For the particular case of CO₂ absorption, the use of a physical approach such as SAFT avoids the need to know the equilibrium constants of the chemical reactions or the concentrations of the product species during the development of molecular models of the relevant compounds. This reduces the degree of uncertainty of those models, as the reaction products are not treated as new species, but in terms of the aggregation of the reactants driven by the presence of strong intermolecular interactions.

Due to the industrial interest of this process, the efforts towards the development of an accurate model to describe the phase behavior of the CO₂ absorption in aqueous MEA are considerable. In most cases, NRTL, UNIFAC and cubic equations of state have been used [30]. Less common, but also employed, is the use of SAFT approaches for mixtures relevant to carbon-capture processes with a good degree of accuracy. The first and pioneering work on this system using a molecular-based approach was the one done by Button et al. [31], who used the original SAFT EoS, describing the molecules as chains of bonded Lennard-Jones segments and running simulations to obtain the dispersion term. They modelled MEA with five association sites, and considered CO₂ as a molecule with 4 association sites. Later on, the statistical associating fluid theory for potentials of variable range (SAFT-VR) [32] was used to model this process using MEA [33] and other multifunctional amines [34]. They described the complex chemistry of CO₂ in amine-based solutions as the equilibria between various species formed at ambient conditions. In these contributions, the multifunctional nature of alkanolamines was taken into account by providing different values to the association sites representing the hydroxyl and amine functional groups, obtaining an accurate representation of the thermodynamic properties and phase equilibria over different pressure, temperature and composition conditions. Also, two effective associating sites were added to CO₂ to describe the chemisorption with the amine group of the alkanolamine. The results provided a satisfactory prediction of the speciation in these systems, in spite of the assumption that key ionic species (the protonated amine and carbamate) were present as tightly bound pairs. This model was later refined and implemented in a process simulator to describe the dynamic non-equilibrium model of a packed column for the chemisorption of CO₂ with MEA [35] and in subsequent optimisation studies. Other thermodynamic efforts related to MEA-based solutions for CO₂ capture are described in detail in the original contribution of Mac Dowell et al. [33] and will not be repeated here. While those studies have shown, in most cases, a good description of the thermodynamics of the ternary mixture involved in the CO₂ absorption step, a considerable number of parameters and binary mixture coefficients are required for this purpose. This fact limits the transferability of the approaches, increasing their uncertainty if, for instance, the amount of MEA in the solution is modified. Very recently, an improved version of SAFT, based on a contribution group (GC) approach coupled into the classical SAFT-VR and named SAFT- γ -SW [36], was used to describe the

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