Thermodynamic characterisation of aqueous alkanolamine and amine solutions for acid gas processing by transferable molecular models

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HIGHLIGHTS

- A robust thermodynamic model of aqueous amines for acid gas removal is proposed.
- Molecular models of amines with different structures are developed.
- Model parameters are transferred from different chemical substances.
- Properties of single/blended amines are described over a broad range of conditions.
- Proposed models reduce the uncertainties associated with solvent properties.

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ABSTRACT

The development of new alkanolamines/amines is a topic which has attracted a great deal research interest, particularly as absorbents for the removal of acid gases from industrial sources and CO_2 capture applications. One of the major challenges when evaluating the techno-economic performance of selected new single amines or blends is the lack of experimental data on the thermophysical properties required for a reliable process design and simulation. In this contribution, a robust theoretical framework for the description of key thermophysical properties of aqueous solutions of single and mixed alkanolamines/amines at relevant gas separation process conditions is proposed. The approach is based on the coupling of the Free-Volume Theory and the Density Gradient Theory with a molecular-based equation of state (soft-SAFT) for the integrated modelling of phase behaviour, enthalpies, densities, viscosities and interfacial tensions. The alkanolamines and amines investigated differ in their family and structure, and included primary (monoethanolamine), secondary (diethanolamine), tertiary (methyldiethanolamine), sterically hindered (2-amino-2-methyl-1-propanol) and cyclic amines (piperazine). The study was performed in a systematic manner, starting from the development of the models for the pure amines, the description of their thermophysical properties, and the properties of the aqueous mixtures. Compared to other models described in literature, the present modelling approach preserves the effects due the chemical structure and key intermolecular interactions of the examined alkanolamines/amines through a set of molecular parameters obtained from pure substance data, whenever available, or transferred from substances of different chemical families. This enabled the development of a consistent modelling framework which can provide reliable thermodynamic property predictions of both single and blended amine solutions over a broad range of temperatures (298–373 K) and compositions (0–50 wt% amine). The proposed approach is well-suited for implementation and extension to other alkanolamines and amines, making it a valuable tool for having reliable process simulations as well as for the screening and discovery of new amine systems, which will be required for the deployment of more economical acid gas removal processes.

1. Introduction

A wide variety of aqueous solutions of alkanolamines has been proposed and studied as solvents for the removal of acid gases, such as carbon dioxide (CO_2) and hydrogen sulphide (H_2S), from industrial sources through an absorption-desorption process [1]. This process

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takes advantage of the reversible nature of the reaction of alkanolamines with acid gases. It involves contacting the acid gas with aqueous solutions of alkanolamines in an absorption column at near ambient conditions and transferring the gas-enriched solution to a second column, known as stripping column, for regeneration at a temperature typically between 373 and 393 K [2,3]. The regenerated solution is recycled back into the absorption column and the purified acid gas is obtained at the top of the regeneration column. Both absorption and regeneration steps are carried out in packed columns for an improved surface area between the gas and the liquid, and operated in a typical counter current flow. This technology is mature and well-understood, having been widely applied to separate CO_2 from natural gas and hydrogen since it was first patented in 1930 [4], and is considered the most prominent technology to be deployed for post-combustion CO_2 capture [2]. However, the elevated energy penalty associated with the solvent regeneration [5,6], as well as the degradation of alkanolamines in the presence of oxygen, equipment corrosion and the environmental impact of potential alkanolamine emissions, still pose as major barriers to the application of this technology at large scale, in particular to flue gas [7]. In this sense, the development of more economical and less energy-intensive acid gas capture processes, with reduced environmental impact, relies on the selection of the best solvents, as it is precisely the chemistry and thermophysical properties of the solvent which determine the overall performance and cost of these processes.

Several recent works have focused on the study of key process design parameters that affect the system's efficiency and cost, including the absorber inlet temperature, solvent inlet flowrate and temperature, gas loading, alkanolamine concentration, humidity in the inlet gas, stripper operating pressure and cumulative energy requirements, as well as different process configurations [6,8–21]. However, fewer studies have addressed the impact of thermophysical properties [22–25] on the final performance of the process, in spite of their importance for its techno-economic feasibility. Kvamsdal and Rochelle [22] performed a sensitivity analysis to evaluate the impact of different correlations for the liquid phase density, heat capacity and mass transfer coefficient on the simulation results. Later, in the same spirit, Kvamsdal and Hillestad [23] investigated different correlations for estimating the liquid phase properties, including density and viscosity, and mass/heat transfer coefficients, and their impact on the predictions of a rate-based absorption model, with results being compared to simulations based on two pilot plants. Nookuea et al. [24] studied the impact of thermophysical properties on the absorber column design and found that, in terms of properties of the liquid phase, the density and viscosity have a significant impact on the packing height and annual capital cost. The authors calculated an overestimation of $1.4 million and an underestimation of $1.0 million in the annual capital cost (AC) of the absorption column for a 400 MW coal-fired power plant due to a 10% underestimation in the liquid density and viscosity, respectively, corresponding to a change of $+7\%$ and -5%, respectively, from the base AC. Other liquid properties which also affected the packing height included diffusivity, interfacial tension and heat capacity. More recently, the model of Mota-Martinez et al. [25] showed the viscosity of the solvent, in addition to the gas loading capacity and reaction kinetics, as the most important properties contributing to the overall cost of CO_2 capture with amine-based solvents.

Among the existing alkanolamines, monoethanolamine (MEA), a primary amine, has been the preferred solvent for industrial gas purification processes [1], with 30/70 wt% MEA/H_2O being the gold standard to which alternative sorption materials are benchmarked. MEA has high gas loading capacities and fast reaction kinetics, which are crucial for an efficient and effective removal of acid gases. However, it also has some important disadvantages, such as high heats of absorption, leading to higher regeneration energy requirements, the formation of irreversible reaction products with carbon sulphide (COS) and carbon disulphide (CS_2), and the presence of highly corrosive solutions at high gas loadings, narrowing the operating range of partial pressures of acid gas or requiring the use of corrosion inhibitors [1]. Moreover, MEA shows a comparatively higher degradation and volatility than solutions of most other amines [1,26,27], significantly increasing the environmental concerns and the costs of the process due to solvent losses. Other alkanolamines of practical industrial interest include diethanolamine (DEA), a secondary amine, methyldiethanolamine (MDEA), a tertiary amine, and 2-amino-2-methyl-1-propanol (AMP), a sterically hindered amine. DEA, MDEA and AMP have in common higher gas absorption capacities and lower energy of regeneration than MEA, but they suffer from slower kinetics [28]. More recently, piperazine (PZ), a cyclic diamine, has attracted a great deal of research attention, being labelled as the new standard for CO_2 capture technology, mostly due to its high reaction rate, resistance to oxidative and thermal degradation, and lower volatility than solutions of MEA [29]. The reader is referred to the study of El Hadri et al. [28] for a more detailed discussion on the characteristics of new amine systems.

The inherent limitations of pure amine systems have led to the development of amine blends as an attractive and easy way of combining the strengths of individual amines. For example, high gas loading capacities of MDEA and AMP can be combined with the high reaction rates of MEA and PZ, and the most important solvent properties can be tailored by varying the relative concentration of each amine. In this context, several blends have been suggested as promising alternative solvents for acid gas separation processes [19,28,30–34].

Given the range of possible amines and formulations, there is a need for developing an accurate and consistent method for predicting the phase behaviour and thermophysical properties of aqueous alkanolamine and amine solutions as a first step towards developing alternative solvents for acid gas removal. Empirical correlations to estimate properties such as density, viscosity, heat capacity and interfacial tension have been proposed among others by Weiland et al. [35,36], Vázquez et al. [37,38] and Jayarathna et al. [39]. Despite providing good results, these correlations are limited to a range of conditions and properties, and are available only for few alkanolamines. Moreover, their extension to the study of new systems of single amines or blends, where no experimental data are available, may lead to erroneous results due to the lack of physical basis of most correlations. Specifically, most of them fail to correctly consider the interactions of the functional groups, which is essential to gain a better understanding of the solvent properties and their impact on the removal of acid gases. A more rigorous approach consists on using a model based on an equation of state (EoS), in particular a molecular-based EoS, to describe the phase non-idealities of these mixtures by taking into account the structure of the molecules and the groups integrating them from the inception of the theory. Molecular-based EoSs derived from the Statistical Association Fluid Theory (SAFT) [40,41] are well-suited for this purpose, thanks to their robustness and physical basis.

In the framework of SAFT, effects due to the chemical structure of molecules and key intermolecular interactions on bulk properties are captured within the theory by a set of molecular parameters. These parameters have a well-defined physical meaning (size of the groups integrating the molecule, chain length, energy of interaction between groups, etc.) and are independent of the fitting conditions. Strong association effects between molecules (*e.g.*, hydrogen-bonding) can be explicitly modelled by the introduction of association site-site pairs, each with a characteristic association strength [40,41]. Such modelling treatment facilitates taking into account the multifunctional nature of alkanolamines due to the presence of hydroxyl and amine groups, and consequently, providing a more reliable representation of key competing intermolecular interactions contributing to the fluid non-ideality. Indeed, SAFT-type EoSs have increasingly become a popular choice for modelling not only the phase behaviour of pure alkanolamines and their aqueous mixtures, but also the chemisorption of CO_2 and H_2S [42–52]. However, whilst a good description of the phase behaviour was obtained in most of these works, the study of the capabilities of the thermodynamic models for describing other key