MODELING MIXTURES OF AMINES AND ALKANOLAMINES WITH THE CPA EQUATION OF STATE

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ABSTRACT

The modelling of amine mixtures is important for many applications, but especially for the processes related to CO_2 capture using aqueous amine solvent systems. In this study, the Cubic-Plus-Association Equation of State (CPA EoS) is used to model amine and alkanolamine mixtures with other fluids such as hydrocarbons, alcohols, chloroalkanes, water and CO_2. Initially, the amine pure fluid parameters were estimated by adjusting model predictions to experimental vapor pressures and liquid densities, assuming two association sites on every amine (2B association scheme) and four association sites on every alkanolamine molecule (4C association scheme). Subsequently, the model was applied to describe the vapor-liquid equilibrium (VLE) of binary systems of amines and alkanolamines with hydrocarbons, alcohols, chloroalkanes and water using one binary interaction parameter, k_{ij}, in most cases. Finally, the model was applied to describe the VLE of typical solvent systems used in CO_2 capture applications, such as the CO_2 systems with aqueous ethanolamine (MEA), *N*-methyldiethanolamine (MDEA) and 3-amino-1-propanol (MPA) solutions, using the pseudo chemical reaction approach, i.e., to account for chemical interactions as very strong specific intermolecular interactions. The latter is a crude approximation, but necessary for applying equation of state models. It was found that the model satisfactorily describes the experimental data using four to six parameters for the CO_2 - alkanolamine interactions, which, however, are less than the number of adjustable parameters in similar literature models.

KEYWORDS: Amines, Alkanolamines, CO2 capture, CPA equation of state

INTRODUCTION

The modeling of amine mixtures is important in many applications of the chemical industry, such as the production of synthetic thermoplastics, agro-chemicals, dyes, anticorrosion agents, drugs or processes with organic solvents. Their physical and chemical properties mainly depend on their strong electron donating capability and their ability to form hydrogen bonds[1]. Thus, the modeling of amine mixtures with other fluids, such as water, hydrocarbons or alcohols, is usually performed with equation of state models capable of accounting the formation of self- and cross- intermolecular hydrogen bonds. Recently aqueous amine solutions received attention due to their ability to chemically absorb acid gases, and especially CO_2, in various separation processes suggested for the mitigation of the climate change[2].

However, modeling the absorption of CO_2 in aqueous amine solutions is a demanding task and, consequently, usually empirical models are used. The rigorous thermodynamic modeling of such reactive mixtures requires simultaneously accounting for the established chemical and phase equilibrium. Thus, it requires the knowledge of the equilibrium constants, which are usually correlated as functions of temperature by adjusting three or four parameters to experimental data, on the top of other pure and binary parameters of the model. The existence of ionic species inside the CO_2 loaded aqueous solution imposes the use of models capable of accounting for ionic interactions, while the large number of such ionic and molecular species imposes the use of many pure fluid and binary model parameters. Nevertheless, if models are adequately parameterized very

useful and satisfactory correlations are obtained[2].

The complexity of the chemical phenomena and the interactions between the various species in the aqueous solutions results in modeling approaches based on severe simplifications. The most popular one is accounting for the ionic interactions as strong specific interactions, such as the Lewis acid-base interactions or the hydrogen bonds. Such pseudo-chemical reaction approach was used by Rodriguez et al.[3] to correlate the absorption of CO_2 in aqueous amine solutions using the SAFT-VR model, while more recently, Perdomo et al.[4] and Papadopoulos et al.[5] applied the same approach, using a group contribution SAFT-γ- Mie equation of state, to predict the phase behavior, including the vapor-liquid-liquid equilibrium, of various phase change amine solvents. Using the Cubic-Plus-Association (CPA) equation of state, such approach was applied by Wang et al.[6], Leontiadis et al.[7], Chen et al.[8] and Tzirakis et al.[9] to model the solubility of CO_2 in aqueous alkanolamine solutions.

THE CPA EQUATION OF STATE

The Cubic-Plus-Association (CPA) equation of state is a combination of the SRK equation of state with the association term of the SAFT type models[10,11]. In terms of pressure it is written as follows[11]:

$$P = \frac{R \cdot T}{V_m - b} - \frac{a(T)}{V_m \cdot (V_m + b)} - \frac{1}{2}\frac{R \cdot T}{V_m}\left(1 + \rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \cdot \sum_{A_i} \cdot \left(1 - X_{A_i}\right) \tag{1}$$

where P is the pressure, V_m the molar volume, T the temperature, $a_i(T)$ is a Soave – type relation for the temperature dependency of the interaction energy and b is the co-volume parameter. X_A represents the fraction of sites A of molecule i that are not bonded with other active sites, while x_i is the mole fraction of component i. X_{Ai} is related to the association strength between two sites belonging to two different molecules, *e.g.* site A on molecule i and site B on molecule j, and is determined from[11] as follows:

$$X_{A_i} = \frac{1}{1 + \rho \cdot \sum_j x_j \sum_{B_j}(X_{B_j} \cdot \Delta^{A_i B_j})} \tag{2}$$

where the association strength Δ^{AiBj} is given by the following relation[10,11]:

$$\Delta^{A_i B_j} = g(V_m)\left[exp\left(\frac{\varepsilon^{A_i B_j}}{R \cdot T}\right) - 1\right]b_{ij} \cdot \beta^{A_i B_j} \tag{3}$$

In the previous expression, $g(V_m)$ is the radial distribution function. The ε^{AiBj} and β^{AiBj} parameters are called the association energy and the association volume, respectively. Such parameters are only used for associating components, and together with the three parameters of the SRK term (a_0, b, c_1), they comprise the five pure compound parameters of the model [10,11]. They are usually obtained by fitting the predictions of the model to pure fluid vapor pressure and liquid density data. For non self-associating components, e.g., hydrocarbons, only the three parameters of the SRK term are required.

RESULTS AND DISCUSSION

Pure Fluid Parameters

Amine pure fluid parameters were obtained by adjusting model predictions to vapor pressures and liquid density data obtained from the DIPPR database[12]. Primary amines present one hydrogen bonding acceptor and two hydrogen bonding donors in their molecules, while secondary amines

present one acceptor and one donor. However, since the amine hydrogen bonds are rather weak, it is not likely that many primary amine molecules simultaneously form three hydrogen bonds. Also, it was observed that accounting in both cases only for one hydrogen bonding acceptor and one hydrogen bonding donor is enough for satisfactory correlations of the pure fluid properties. For this reason, both primary and secondary amines were modeled using the 2B association scheme. Furthermore, alkanolamines, such as ethanolamine (MEA), *N*-methyldiethanolamine (MDEA) and 3-amino-1-propanol (MPA) were modeled using the 4C association scheme. In all cases, the model satisfactorily correlates the vapor pressures and the liquid densities with absolute average deviations ranging from 0.5-2.5% in most cases. Two characteristic plots are presented in Figure 1 for ethylamine.
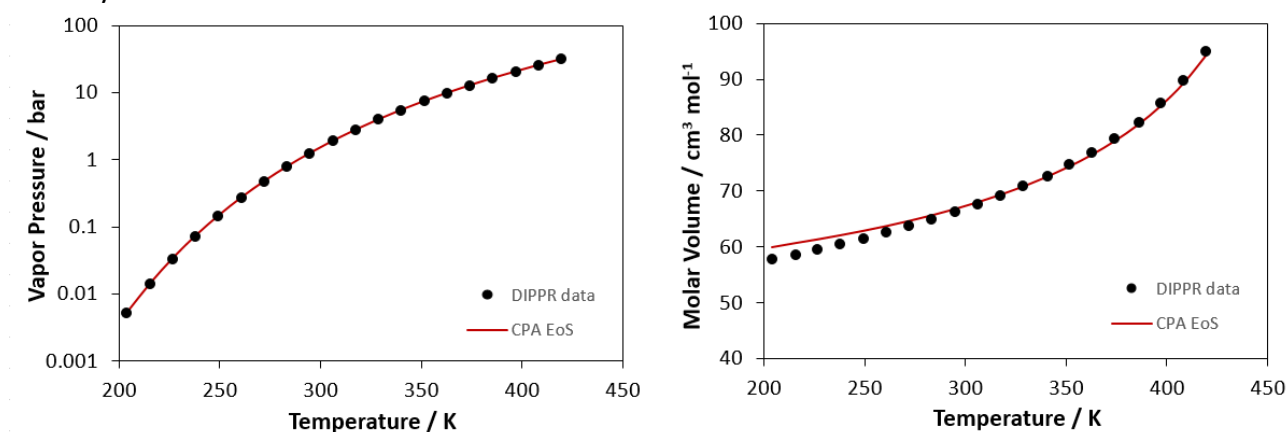

Figure 1. *Ethylamine vapor pressures (left) and molar volumes (right). Data from the DIPPR[12] database and correlations using the CPA equation of state.*
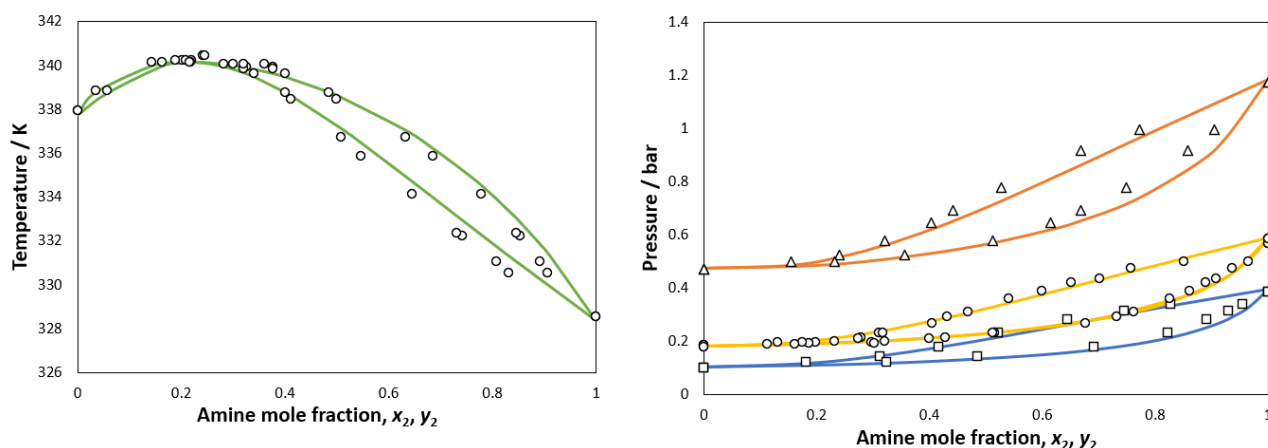
Binary Mixtures

Binary systems of amines and alkanolamines with hydrocarbons, alcohols, chloroalkanes and water were described using one binary interaction parameter, k_{ij}, in most cases. Some typical results for methylamine are presented in Table 1. In the great majority of the studied systems, the average deviations range between 0.5-3 % for the vapor pressure (or the boiling point), while higher deviations are typically observed for the mole fraction of the heavier compound in the vapor phase. Some representative calculations are illustrated in Figures 2 and 3 for methylamine and diethylamine, respectively.

Table 1. *Binary mixtures with methlymanine*

| System	Type of data	Temperature or Pressure range	k_{ij}	%AAD in P (or T)	%AAD in y_1	%AAD in y_2
Methylamine – *n*-Butane	Isothermal *x,P,T*	288 K	0.0347	0.96	-	-
Methylamine – *n*-Hexane	Isothermal *x,y,P,T*	293 K	0.0262	3.38	1.19	7.96
Methylamine – *n*-Nonane	Isothermal *x,P,T*	273-293 K	0.0141	5.22	-	-
Methylamine – Dimethylamine	Isobaric *x,y,P,T*	101.32 kPa	-0.0104	0.05	3.65	2.10
Methylamine – Trimethylamine	Isothermal *x,P,T*	273–293 K	-0.0516	0.69	-	-
Methylamine – Carbon tetrachloride	Isothermal *x,P,T*	253–293 K	-0.0420	2.84	-	-
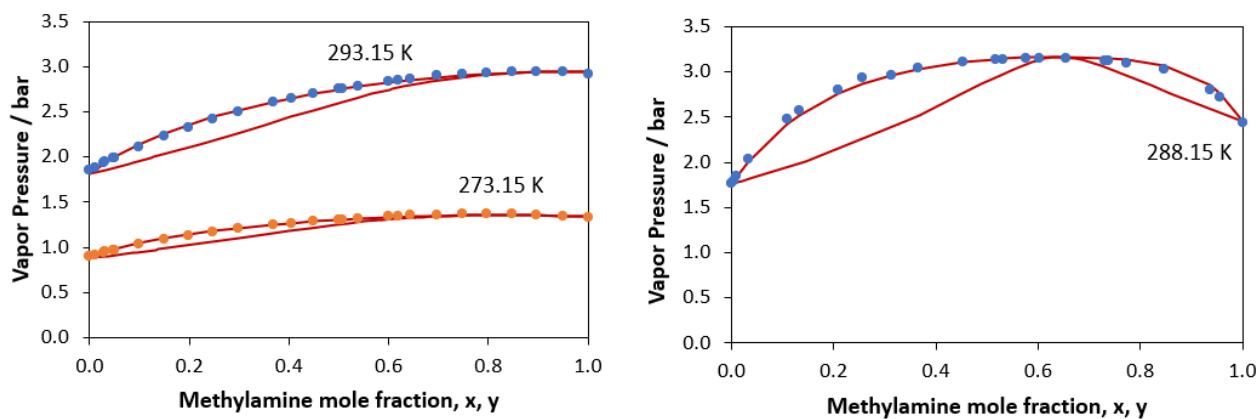
Figure 2. *Methylamine – Trimethylamine VLE (left) and Methylamine-butane VLE (right). Experimental data and CPA calculations.*


Figure 3. *Diethylamine – Methanol VLE (left) and Diethylamine-Ethanol VLE (right). Experimental data and CPA calculations.*

Ternary Mixtures with CO_2

The pseudo chemical reaction approach[3-9], i.e., to account for chemical interactions as very strong specific interactions, was used in order to model the ternary reactive systems that contain CO_2, amines and water. Such approximation arises from the inability of equation of state models to account for chemical interactions. In more detail, alkanolamines were modeled assuming that they have two proton donor and two proton acceptor sites that can form hydrogen bonds (4C association scheme) and one chemical site that can only interact with CO_2. On the other hand, CO_2 was modeled assuming one negative site that can only cross-associate with water[13] and additional chemical sites that can only cross-associate with amines[7,9]. In cases of mixtures with primary or secondary amines, two such chemical CO_2 sites are active and, in this way, the stoichiometric limit of 0.5 moles of CO_2 that can react with one mole of amine groups, which is valid if the carbamate formation is the dominant reaction, is confirmed. On the other hand, only one chemical CO_2 site is active in mixtures with ternary or sterically hindered amines and, in this way, the stoichiometric limit of 1 mole of CO_2 that can react with one mole of amine groups, which is valid if the carbamate cannot be formed or if it is very unstable, is confirmed. An illustration of such pseudo-chemical interactions is presented in Figure 4.
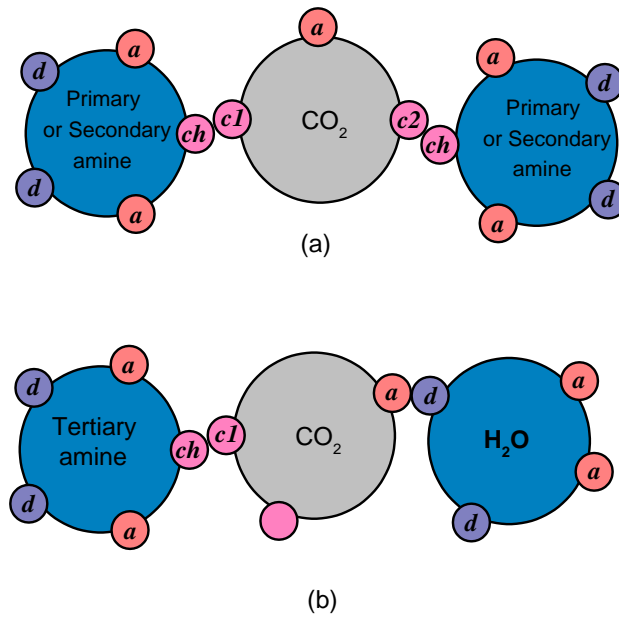
Figure 4. *The pseudo-chemical interactions for primary or secondary amines (a) and tertiary or sterically hindered amines (b). The association sites are presented, i.e. sites for chemical interactions (ch, c1, c2), as well as proton donor (d) and proton acceptor sites (a) capable for hydrogen bonding.*
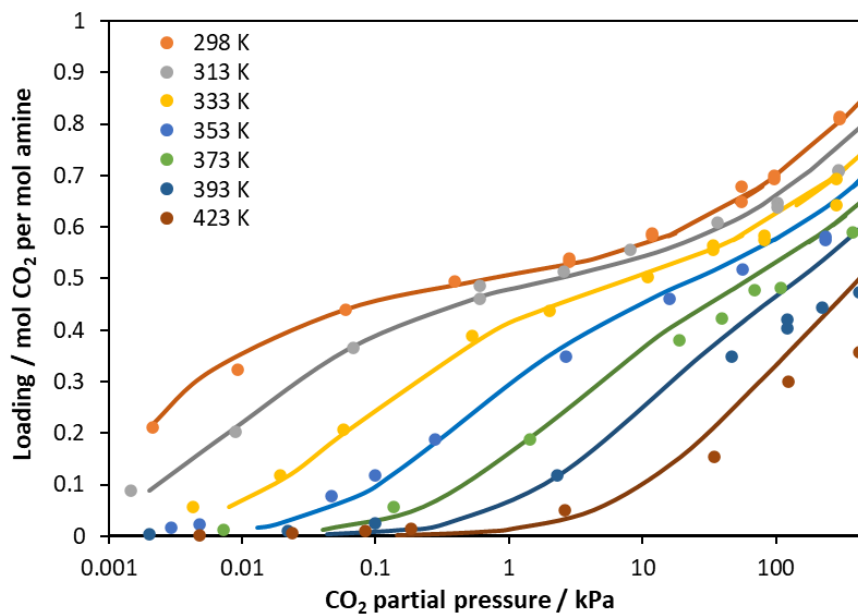
Figure 5. *CO_2 loading of 30%wt. aqueous MEA solution. Experimental data[14] and CPA calculations.*

The model was applied to describe the vapor liquid equlibrium of typical solvent systems used in CO_2 capture applications, such as the CO_2 systems with aqueous ethanolamine (MEA), *N*-methyldiethanolamine (MDEA) and 3-amino-1-propanol (MPA) solutions. Some characteristic results are presented in Figures 5 and 6. In more detail, in Figure 5 the CPA calculations are presented with the experimental data for 30% aqueous MEA solutions of Jou et al.[14], which refer to a broad temperature range (298-323 K) and to CO_2 partial pressures of 10^{-3} - 10^3 kPa. In Figure 6, the model correlations for the CO_2 solubility in aqueous MDEA and MPA solutions, at 313 K, are presented and are compared to literature experimental data. In all cases, rather satisfactory correlations were obtained. More details about the used approach, the model parameters and the obtained results are presented in recent studies[7,9].
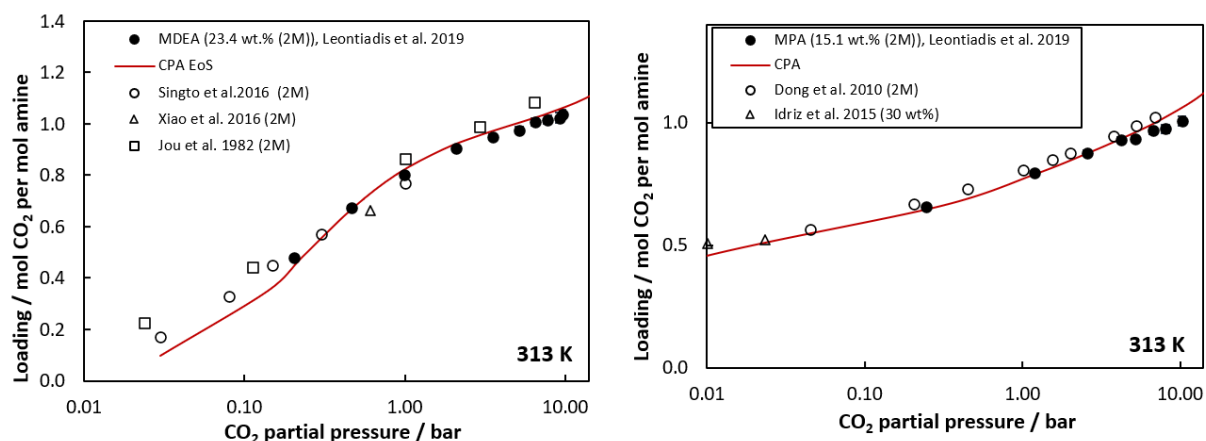
Figure 6. *CO_2 loading of MDEA and MPA aqueous solutions. Experimental data[15-19] and CPA calculations.*

CONCLUSIONS

The Cubic-Plus-Association Equation of State (CPA EoS) was used to model amine and alkanolamine mixtures. Initially, the pure fluid parameters for primary, secondary and tertiary amines, as well as alkanolamines were obtained by adjusting model predictions to experimental vapor pressures and liquid densities. Subsequently, the vapor liquid equilibrium of binary mixtures of amines or alkanolamines with other fluids, such as hydrocarbons, alcohols, chloroalkanes and water, was modeled and the binary parameters of the model (one k_{ij} in most cases) were obtained. Finaly, the model was applied to describe the CO_2 solubility in aqueous ethanolamine (MEA), *N*-methyldiethanolamine (MDEA) and 3-amino-1-propanol (MPA) solutions, using the pseudo chemical reaction approach, i.e., to account for chemical interactions as very strong specific intermolecular interactions. Such thorough parameterization of the CPA model allows the application of the model to a variety of amine systems relevant to the chemical industry and CO_2 capture applications.

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