Modeling of CO_2 solubility in aqueous *N*-methyldiethanolamine solution using electrolyte modified HKM plus association equation of state

CrossMark

Alireza Afsharpour, Ali Haghtalab*

Department of Chemical Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran

ABSTRACT

In this work, a new type of electrolyte cubic plus association equation of state as emHKM-CPA EoS has been developed and was used to modeling the CO_2 solubility in aqueous alkanolamine such as *N*-methyldiethanolamine (MDEA) and diethanolamine (DEA) solutions. This EoS consists of the several terms as the cubic HKM part for dispersion contribution, electrolyte part and association term. The Mean Spherical Approximation (MSA) term together with Born term are used for electrostatic long-range interaction and charging processes, respectively, and for association the Wertheim equation was applied. Using the present EoS, the solubility of CO_2 in aqueous MDEA solutions is modeled so that the 470 experimental solubility data were used at the different solution compositions, temperatures, pressures and acid gas loadings. At first, the pure components parameters were obtained through regression of the pure components vapor pressure and saturated liquid density experimental data. Consequently, the binary interaction parameters were calculated using the binary vapor-liquid equilibrium data. Finally, the ternary H_2O-CO_2-MDEA and H_2O-CO_2-DEA systems were modeled using a reactive bubble point pressure calculation method. Moreover, the present EoS is applied for LLE calculation of heptane-MEA system. The results showed that the calculated values were in good agreement with the experimental data. For the H_2O-CO_2-MDEA and H_2O-CO_2-DEA systems, the percentage of Absolute Average Deviation (AAD%) were 12.14 and 9.17, respectively, that shows emHKM- CPA is an efficient EoS which can be successfully applied to representation of the solubility of CO_2 in aqueous alkanolamine solutions in wide ranges of temperature, pressure, acid gas loading, and amine concentration.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

CO_2 removal from various gas streams is necessary since it has several technical and economic concerns. Moreover, the presence of CO_2 in natural gas leads to decrease its heating value, produces corrosion in equipment, and pipes [1]. Since 1930 [2], the absorption of CO_2 into physical and chemical solvents has been widely used in gas industry so that presently the aqueous alkanolamine systems are economically good choice for acid gas removal [3]. The big advantage of aqueous alkanolamine systems is that the CO_2 absorption is taking placed through physical and chemical mechanisms in the liquid phase so that a high acid gas loading is achieved. Some of the most known suitable alkanolamines are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) that MDEA presents superiority with advantageous of less corrosion, less regenerative energy and good thermal stability [4]. On the other hand, the design of a gas treatment process with alkanolamine-based aqueous solvent requires knowledge of the vapor—liquid equilibria (VLE) of the acid gas—alkanolamine—water system in both experimental solubility data and thermodynamic modeling.

Presently, a large number of experimental VLE data has been given in the literature that needs a proper thermodynamic model which to be used in design and simulation of an acid gas removal unit [5]. Moreover, in a water —CO_2—MDEA system, significant amounts of the different ionic complex species such as the protonated MDEA (MDEAH$^+$) and hydrogen carbonate (HCO$_3^-$) are formed through reactions of CO_2 with alkanolamine in the aqueous phase. The vapor-liquid equilibrium calculation of such acid gas-alkanolamine systems needs explicitly accounting for the

* Corresponding author.
E-mail address: haghtala@modares.ac.ir (A. Haghtalab).

hydrogen bonding effect and ionic interactions, particularly, in the aqueous phase so that they present a huge impact on accurate calculation of the acid gas solubility calculation [6—8]. The different approaches of the phase equilibrium calculation have been used so far that Phi-Phi approach through applying an equation of state is more demanded than Gamm-Phi (activity coefficient) approach. In this method, the same EoS is utilized for both vapor and liquid phases. In a contactor unit to absorb acid gas in a solvent, the process is take placed at high pressures so that the difference between the liquid and vapor phase's densities becomes smaller and may even disappear. Thus, using an appropriate EoS for vapor--liquid equilibrium computation of alkanolamine systems has been highly demanded in recent years [9—13]. In the last few years, a variety of models so called associating models have been presented so that they are capable to take into account hydrogen bonding effect explicitly. These types of models are especially convenient to describing phase equilibria of mixtures containing polar and/or strongly associating compounds [14]. One of the well-known families of such models is SAFT variants that have been widely applied in recent works.

Haghtalab and Mazloumi [10] developed the electrolyte cubic square-well (eCSW) equation of state that was applied to study the CO_2 and H_2S solubility in aqueous MDEA solutions in the wide range of pressure, concentration, temperature, and acid gas loading. The eCSW EoS consists of the mean spherical approximation (MSA) theory, the Born equation, and the cubic square-well equation of state (SWEoS). Using eCSW EoS, the vapor-liquid equilibrium calculations were performed for the binary and ternary systems of the acid gases-alkanolamine systems through the simultaneous calculation of vapor-liquid equilibria and chemical equilibria. Effect of the binary interaction parameters, K_{ij}, on the performance of eCSW EoS was investigated using a large number of experimental data points of the acid gas solubility in aqueous MDEA solutions. The results illustrated that this EoS presents capability to represent the solubility data of both ternary and quaternary aqueous alkanolamine systems with very good accuracy and overall AAD% of 11.6 [11].

At the work of Uyan et al. [4] an electrolyte PC-SAFT EoS was applied to calculate the CO_2 solubility in aqueous MDEA solutions in the range of 313—413 K and loadings of up to 1.32 (mole CO_2/ mole MDEA). The ARD % was 22.9 so that at lower MDEA weight fractions and higher temperatures, the predicted results were in good agreement with the experiment; however the deviations increase with increasing MDEA weight fraction and temperatures lower than 333 K. Button and Gubbins [12] extended the SAFT EoS to fluid hydrogen bonded mixtures. The new parameters were obtained for CO_2 and H_2O to achieve better agreement with the experiment so that a more consistence parameters with the other associated molecules were optimized. The results for the aqueous MEA and DEA systems showed a deviation 1—2% in the predicted component mole fraction and their results for the aqueous CO_2-MEA and CO_2-DEA systems presented the deviation of 0.01 in mole fraction. Najafloo et al. [13] developed eSAFT-HR EoS to modeling the CO_2 solubility in aqueous MDEA solution in a wide range of pressure (2.84—7565 kPa), temperature (298—413 K), MDEA concentration (18.8—50.1 wt%), and CO_2 loading (0.00025—1.31608). A consistent database of the 413 experimental data points was utilized in their work. The overall average absolute percent relative deviation (AAD%) and mean BIAS percent deviation (BIAS%) for the ternary solution were 11.2 and 4, respectively. To validate the results of the eSAFT-HR EoS, the solubility data of Huttenhuis et al. [15] was utilized to model the MDEA—CO_2—H_2O system at 298 K so that the AAD% and BIAS% were 25.6% and 5.5%, respectively [13]. Nasrifar and Tafazzol [16] applied the PC-SAFT EoS to model the acid gases solubility in the aqueous MEA, DEA, and MDEA solutions

so that their results showed a high deviation for the CO_2 + MDEA + water system.

The SAFT type models predict acid gas solubility in alkanol-amine solution with good accuracy, but these statistical associate models are complex. On the other hand, the cubic EoSs are simple, but they present lack of accuracy for hydrogen-bonded systems. To take advantages of these two type equations of state a type of EoS known as Cubic Plus Association (CPA) EoS, which incorporates both cubic and association terms, has been developed in the recent decay. In fact, these kinds of models combine simplicity and accuracy [14]. In CPA EoS the SRK and Werthiem terms are combined, however in the work of Zoghi et al. [17], the PR and association terms are combined with an electrolyte term which is denoted as PR-CPA EoS that was employed to modeling CO_2 solubility in aqueous solutions of MDEA. For the electrolyte part of the model, they used the electrolyte part of the Fürst and Renon [18] model plus the Born term. Using ePR-CPA EoS, for the 336 solubility data the overall AAD% was 17.3. Thus, it seems the cubic term in the CPA type EoS presents a major contribution in improving accuracy of this kind of equations of state. Therefore, in this work to improve accuracy, a new version of CPA EoS is developed as the emHKM-CPA EoS, that the SRK term is replaced by a new term of HKM. In this version of CPA, we incorporate an electrolyte term to calculate solubility of acid gases in aqueous alkanolamine solution in a wide range of acid gas loading, temperature and pressure.

2. Thermodynamic framework

2.1. emHKM-CPA EoS

Following the Cubic Plus Association (CPA) EoS [14], the emHKM-CPA EoS is developed that consists of four terms as follows. The first term is a modified cubic HKM EoS [19] that presents the dispersion contribution. The second term is the association contribution, which is given in the original CPA EoS. To take into account the long-range electrostatic contribution, the mean spherical approximation (MSA) term plus Born term are added to CPA EoS. Thus, the Helmholtz function of the emHKM-CPA EoS is expressed as

$$\left(\frac{A^r}{RT}\right)_{eHKM-CPA} = \left(\frac{A^r}{RT}\right)_{mHKM} + \left(\frac{A^r}{RT}\right)_{Assoc.} + \left(\frac{A^r}{RT}\right)_{MSA} + \left(\frac{A^r}{RT}\right)_{Born} \tag{1}$$

where the HKM term in Eq. (1) is written as [19].

$$\left(\frac{A^r}{RT}\right)_{mHKM} = \frac{a(T)}{RT(mc-nb)} \ln\left(\frac{v+nb}{v+mc}\right) + \ln\left(\frac{v}{v-b}\right) \tag{2}$$

The other terms have been given in the literature [11,14,20].

Having the residual Helmholtz energy, the fugacity coefficient is obtained as

$$\varphi_i = \frac{RT}{Pv} \exp\left(\frac{\mu_i^r}{RT}\right) \tag{3}$$

where μ_i^r, the residual chemical potential of component "i", is written as

$$\frac{\mu_i^r}{RT} = \left(\frac{\partial\left(A^r/RT\right)}{\partial n_i}\right)_{T,V,n_{j\neq i}} \tag{4}$$

The parameters of the mHKM term are calculated as