Solubility of Carbon Dioxide in Aqueous Blends of Piperazine and N-Methyldiethanolamine

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Abstract

In the present work, new experimental data are reported on the equilibrium solubility of carbon dioxide into aqueous mixtures of N-methyldiethanolamine (MDEA) and piperazine (PZ). The experimental results are generally well in line with existing experimental data. Also, the newly obtained and existing experimental VLE data on this system have been correlated with the use of an Electrolyte Equation of State. It was found that the thermodynamic model derived was able to describe the CO_2-H_2O-PZ-MDEA system reasonably well over a wide range of conditions.

Keywords: CO_2, solubility, equilibrium, piperazine, MDEA, equation of state

Introduction

The removal of carbon dioxide from process gas streams is frequently carried out with an absorption / desorption technology, using (aqueous) solutions of (alkanol)amines as reactive solvent. Nowadays, it is common to add (small amounts) of 'promotors' to aqueous solutions of (alkanol)amines, such as piperazine (PZ) in aqueous N-methyldiethanolamine (MDEA). The basic principle behind this development is to enhance the rate of absorption via the relatively high rate of reaction of PZ with CO_2, while maintaining the low heat of regeneration in the stripper section, stemming from the relatively low heat of reaction of MDEA with CO_2. Requirements for an optimal design and operation of both absorber and stripper are detailed information on the mass transfer characteristics, the kinetics of the reactant(s) with CO_2, and detailed knowledge on the thermodynamics of the solvents.

Therefore, the present paper presents experimental data on the solubility of carbon dioxide into aqueous solutions of MDEA blended with PZ, which are complementary to the data sets already available in literature [2,10,14,15,19]. Next, the total set of experimental data, originating from this work and literature, are used to develop a thermodynamic model based on the electrolyte equation of state (EoS), as originally introduced by Fürst & Renon [6]. The application of this EoS based model is a relatively new approach for describing acid gas solubilities in aqueous (alkanol)amine systems. One of the major advantages is the use of identical equations for describing both the liquid and the gas phase, as – among others – pointed out by Solbraa [16].

Experimental

The experimental setups and procedures are almost identical to the ones applied in the preceding work of Derks et al. [5] on the ternary system CO_2-PZ-H_2O, and will therefore not be explained in detail here. One modification has been made to the experimental setups: both a conductivity meter and a pH electrode have been included in the system by means of a sampling loop in the reactor part, in order to obtain additional information on the speciation of the liquid phase.

As in the previous study, experimental data have been obtained using two different setups/modes of operation, depending on the desired CO_2 equilibrium partial pressure. Solubility data with carbon dioxide partial pressures lower than ca. 10 kPa were obtained using the continuously operated setup, whereas a batchwise type of operation was applied for experiments targeted at CO_2 equilibrium partial pressures ranging from 10 to about 100 kPa.

Electrolyte Equation of State

General

As mentioned in the introduction, the Electrolyte EoS will be applied to describe the CO_2 solubility into aqueous solutions of piperazine and MDEA. In this EoS approach, the system's non-ideality is given as the sum of four different molecular and ionic contributions to the reduced Helmholtz free energy A^R, as given in Equation 1:

$$\left(\frac{A-A^{IG}}{RT}\right)=\left(\frac{A^R}{RT}\right)=\left(\frac{A^R}{RT}\right)_{RF}+\left(\frac{A^R}{RT}\right)_{SR1}+\left(\frac{A^R}{RT}\right)_{SR2}+\left(\frac{A^R}{RT}\right)_{LR} \qquad \text{Eq 1}$$

Governing equations for the molecular interactions, which include both repulsive forces (RF) and short range interactions (SR1), and the ionic (short range, SR2, and long range, LR) contributions, are listed in the previous work [5]. For the present study, the model from the previous work, which was used to successfully describe the CO_2 solubility in aqueous piperazine solutions, was extended to include the tertiary alkanolamine MDEA. Basically, the EoS model for the quaternary MDEA-PZ-H_2O-CO_2 system can be represented as a tree structure consisting of the subsystems involved, as illustrated in Figure 1.
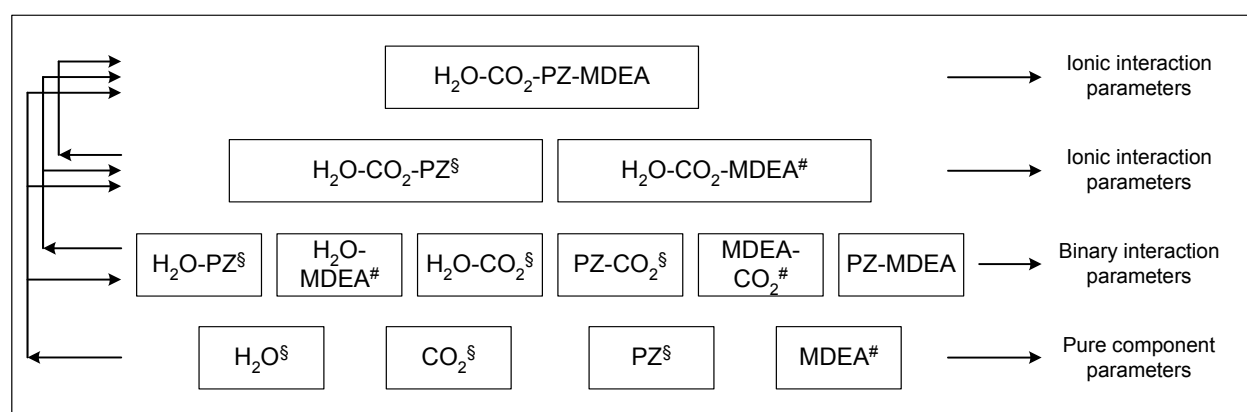

Figure 1. Schematic buildup of the equilibrium model.

As one can see from Figure 1, the final (quaternary) model requires (sets of) parameters which are to be determined from the various subsystems present in the tree structure. Furthermore, it is obvious that many parameters necessary for the final model fit, are also part of the ternary (reactive) system PZ-CO_2-H_2O which has been studied by Derks et al. previously [5]. For information on these sets of parameters (marked with § in Figure 1) and their respective values is therefore referred to [5].

MDEA-CO$_2$-H$_2$O

The majority of the remaining, unknown, parameters (marked with # in Figure 1) are a part of the second ternary system, consisting of MDEA, carbon dioxide and water. As in the previous study, the molecular pure component and binary interaction parameters were determined by fitting them to experimental (VLE and/or freezing point depression) data, with the exception of the MDEA-CO_2 interaction. Values and experimental data sources are listed in Table 1, along with the MDEA (molecular) and MDEAH$^+$ (ionic) diameters. MDEA's critical constants were taken from Chunxi et al. [4].

With respect to the implementation of the model describing the ternary MDEA-CO_2-H_2O system – and the subsequent regression of the required ionic interaction parameters – the following remarks should be made:
- The presence of both the H_3O^+ and the CO_3^{2-} ion has not been taken into account, because their concentrations are negligibly low;

- Interactions between ions of equal charge, as well as between anions and molecules, have been neglected;
- The reference state for all species in solution, with the exception of water, is infinite dilution in water, and the corresponding equilibrium constant for the MDEA protonation reaction has been (after conversion to the mole fraction scale) taken from Pérez-Salado Kamps & Maurer [13].
- The database used in the regression of the ionic interaction parameters on the MDEA-CO_2-H2O system was identical to the one used by Huttenhuis et al. in their work [9].

Table 1. Parameters used in the modelling of the MDEA-CO_2-H_2O equilibrium.

Single component parameters		Binary systems	
MDEA		**H$_2$O – MDEA**	
p_1	0.5244	$\Delta'g_{12}$ [kJ mol^{-1}]	26.26
p_2	-1.1529	$\Delta''g_{12}$ [J mol^{-1} K^{-1}]	-91.5
p_3	0	$\Delta'g_{21}$ [kJ mol^{-1}]	-13.52
source	[12]	$\Delta''g_{21}$ [J mol^{-1} K^{-1}]	50.5
Molecular diameter [·10^{-10} m]	4.50	$\alpha_{12} = \alpha_{21}$	0.27
Source	[4,5,16]	Source	[3,17,18]
MDEAH+		**MDEA – CO$_2$**	
Ionic diameter [·10^{-10} m]	4.50	Interaction parameter k$_{mix}$	0.2
Source	[4,16]	Source	[16]

The EoS-model was able to correlate the experimental data used in the regression with an average absolute deviation of 26 %, which is comparable to other studies, which applied the Electrolyte EoS model to describe CO_2 solubilities in aqueous MDEA solutions. The obtained values for the ionic interaction parameters are listed in Table 2 and a graphical comparison between the experimental solubilities included in the database and model prediction is given in Figure 2.

Table 2. Ionic interaction parameters for the MDEA-CO_2-H_2O system.

W_{ij}	10^3 m^3 mol^{-1}
MDEAH$^+$ - H$_2$O	0.1189
MDEAH$^+$ - MDEA	0.0756
MDEAH$^+$ - CO$_2$	-0.0705
MDEAH$^+$ - HCO$_3^-$	-0.1473

Figure 2. Parity plot for the MDEA-CO_2-H_2O system.

The extension to the final model containing both piperazine and MDEA will be discussed in the 'Results' section, after the newly obtained experimental data have been presented.

Results

Experimental results

Before the equilibrium experiments into aqueous blends of piperazine and MDEA were carried out, the experimental setup was experimentally validated by measuring the CO_2 solubility in aqueous solutions of 2.0 kmol MDEA at 313 K. Results are shown graphically in Figure 3.
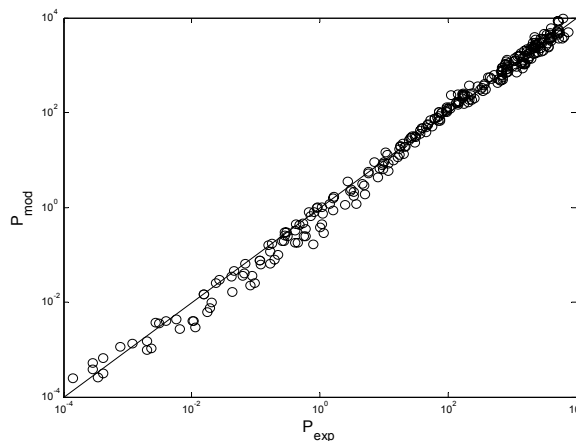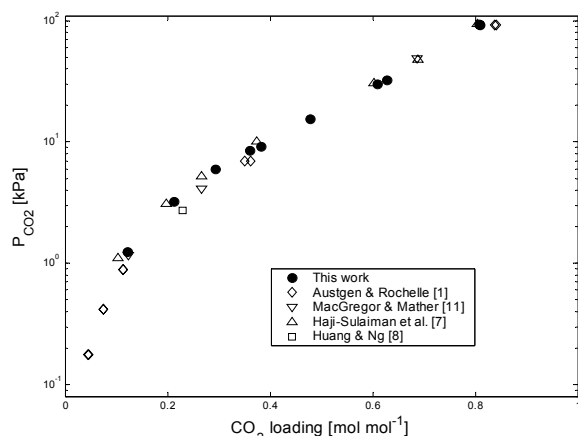
Figure 3. CO_2 solubilities in 2.0 kmol m^{-3} aqueous MDEA solution at 313 K.

From Figure 3, it can be concluded that the data from the setup are in good agreement with literature data, and that the addition of the sampling loop has no influence on the outcome of the experiments. Next, CO_2 solubility experiments have been carried out with aqueous solutions containing 2.8 M MDEA and 0.7 M PZ, at temperatures of 30 and 50 ºC. These conditions were chosen to compare and extend one of the equilibrium dataseries of Liu et al. [10], who report CO_2 partial pressures ranging from about 15 to 450 kPa at these conditions. The newly obtained experimental data are shown in Figures 4a&b. A comparison to the data reported by Liu et al. [10] is given in Figure 4b.
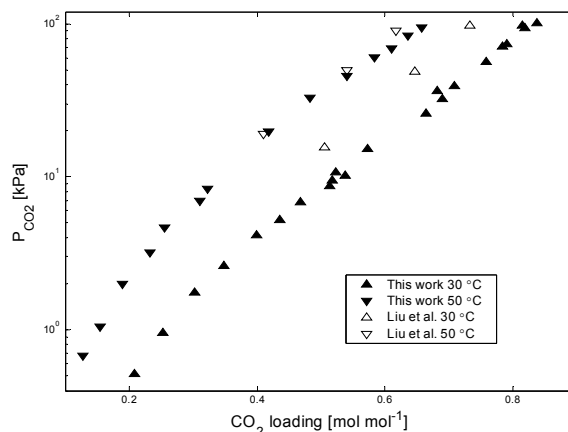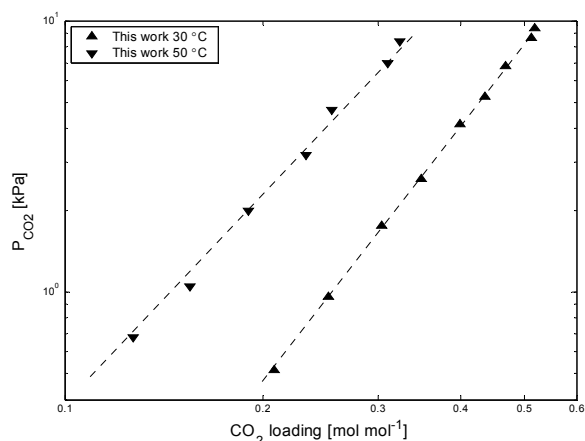
Figures 4a&b. Experimental CO_2 solubilities in aqueous solutions of 2.8 M PZ and 0.7 M MDEA.

From Figures 4a&b, it can be concluded that the experimental data at 50 ºC are well in line with those of Liu et al. [10]. However, there seems to be a discrepancy between the two data sets at 30 ºC. Secondly, the log-log plot (Figure 4a) shows a linear relation between the partial pressure and the loading for the experimental data taken at low CO_2 partial pressures, which is expected at low loadings (see e.g. [4]) and thus proves that they are internally consistent.

Modelling results
Next, an attempt was made to regress the remaining (quaternary) ionic parameters to the available experimental CO_2 solubilities in aqueous blends of piperazine and MDEA. Also the binary interaction parameter k_{mix} describing the PZ-MDEA interaction was adjusted, since the model turned out to be very sensitive to its value. The results of the regression are shown graphically in the parity plot given in Figure 5.
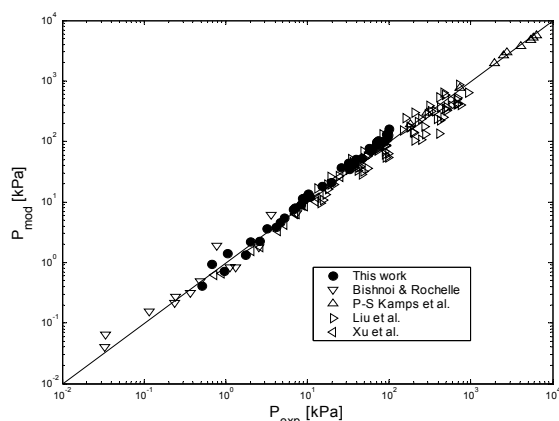
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Figure 5. Parity plot for the PZ-MDEA-CO_2-H_2O system.

Now, the experimental speciation data of a partially loaded PZ-MDEA solution, obtained via NMR spectrometry, as reported by Bishnoi & Rochelle [2], are compared to the model prediction in Table 6.

Table 6. Comparison between experimental speciation data and model prediction, in a 1M PZ, 3 M MDEA solution with a 0.52 loading at 298K.

Fraction	NMR value [2]	Model prediction
$PZ(COO^-)_2$ / $(MDEA + MDEAH^+)$	0.12	0.21
$PZ(COO^-)_2$ / $(PZCOO^- + {}^+HPZCOO^-)$	0.63	2.7
$(PZCOO^- + {}^+HPZCOO^-)$ / $(PZ + PZH^+)$	4.1	1.9

It can be concluded from Figure 5, that the present model is able to nicely correlate all experimental solubility data, with an average absolute deviation of less than 25 %. However, the model was not able to predict the experimentally obtained speciation results of the single available speciation data point, as shown by Table 6.

Conclusions

The present study reports experimental data on the solubility of CO_2 in aqueous solutions of 2.8 M MDEA and 0.7 M piperazine at 30 and 50 ºC. After validating the experimental setup and procedure with the well known MDEA-CO_2 system, new experimental data were measured. The obtained experimental data were found to be internally consistent and well in line with the results of Liu et al. [10] at 50 ºC. However, VLE data taken at 30 ºC were found to deviate from the values reported by Liu et al.. The thermodynamic model used, based on the Electrolye Equation of State, was able to predict the experimental data over a wide range of conditions, despite various simplifications and assumptions made in the implementation of the model.

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