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Binary and ternary VLE of the 2-(diethylamino)-ethanol (DEEA)/3-(methylamino)-propylamine (MAPA)/water system

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HIGHLIGHTS

- Binary, ternary VLE data measured for DEEA/H_2O, DEEA/MAPA and DEEA/MAPA/H_2O.
- Titration technique developed to quantify the DEEA/MAPA system.
- The UNIQUAC framework implemented and the parameters are fitted.
- Activity coefficients of DEEA/MAPA in ternary found lower than for binary systems.
- An inconsistency seen between water activity coefficients from VLE and SLE results.

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ABSTRACT

A mixed 2-(diethylamino)-ethanol (DEEA) and 3-(methylamino)-propylamine (MAPA) system could be an attractive alternative solvent to improve the performance of CO_2 capture for low partial pressure cases. This solvent has the advantages of forming two liquid phases upon CO_2 loading, one rich in CO_2 and the other very low in CO_2. Having a highly concentrated rich solvent improvements could be reached by reducing the sensible heat and improving the equilibrium sensitivity hence reducing the need for stripping steam. Also it is possible that the heat of absorption may change to the better.

To better understand this system in designing the separation unit requires substantial work on characterization of the solvent. One important aspect is to provide equilibrium data. In this work new ebulliometric VLE data for the binary DEEA/H_2O and DEEA/MAPA systems and the ternary DEEA/MAPA/H_2O system are reported at different temperatures and concentrations. Results show that pure MAPA is more volatile than DEEA, but in aqueous solution MAPA was found to be less volatile. A mix of DEEA and MAPA in aqueous solution tends to lower the volatility thus makes the system more advantageous by reducing volatility. The activity coefficients for the species in the ternary aqueous system are found to be lower than the activity coefficients obtained from the corresponding binary aqueous mixtures.

The UNIQUAC framework was implemented to represent the experimental data. The six UNIQUAC parameters were determined and were able to predict *P-T-x-y*, activity coefficient, excess enthalpy and freezing point depression for both the binary and ternary systems. However, a small inconsistency was observed between water activity coefficients determined from ebulliometer and freezing point depression measurements.

1. Introduction

Amine mixtures which potentially form two phases at higher CO_2 concentration have recently received attention as a CCS technology. The changes in technology comprises two major elements, solvent and process development. When two phases occur the regeneration heat requirement could be expected to be lower as only a lower phase, being a highly concentrated rich solvent is sent to the stripper and the sensible heat loss could be reduced. By forming a second phase the equilibrium temperature sensitivity could be improved thereby reducing the need for stripping steam and also the heat of absorption may be affected positively.

The DMX process by IFPEN is based on special solvents forming two immiscible phases and is now under testing in Italy (Raynal et al., 2011). This process is claimed to give a specific reboiler duty as low as 2.1 GJ/tonne CO_2 captured which is significantly lower than

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the 3.0–3.7 GJ/t CO_2 reported for the modified and classical 30 wt% MEA reference processes. Another process with two liquid phases is based on a thermomorphic biphasic solvent type. It gives a single phase at lower temperature but two phases at higher temperature (Zhang, et al., 2011). The advantage of this solvent was to adopt it to a concept where regeneration of the solvent can take place without steam.

A blend of 2-(diethylamino)-ethanol (DEEA) and 3-methylamino)-propylamine (MAPA) having characteristics of a biphasic/phase change solvent is now intensively studied at NTNU within the EU iCap project. At very low CO_2 loadings, this solvent behaves as a single phase but at higher CO_2 loadings it gives two phases. For design and modeling of this gas treating process the knowledge of vapor–liquid equilibrium (VLE) of the mixed amine/CO_2/water system is required. At low CO_2 gas concentrations the phase equilibrium is governed by the binary/ternary DEEA/MAPA/water system.

DEEA is a tertiary alkanolamine, which has received interest by different researchers both as pure and in aqueous solution. Among data available are heat of reaction of CO_2 (Kim, 2009), freezing point depression (Arshad et al., 2013), kinetic absorption CO_2 rate (Konduru et al., 2010; Vaidya and Kenig, 2009), viscosity (Maham, et al., 2002), density (Lebrette et al., Mather), excess enthalpy (Mathonat et al., 1997) and vapor pressure (Klepáčová et al., 2011; Kapteina et al., 2005; Steele et al., 2002).

MAPA is diamine which has one primary and one secondary amine group attached. It would be expected to have fast absorption kinetics. Reports on characterization of MAPA both as pure and in aqueous solution are limited. Data available are: heat of reaction of CO_2 (Kim, 2009), vapor pressure and binary aqueous MAPA VLE data where two different thermodynamic models were developed, i.e. Wilson and NRTL (Kim et al., 2008). Aronu (2011) implemented the UNIQUAC model to these data. Other data are freezing point depression (Arshad et al., 2013) and vapor pressure of MAPA at very low concentrations (Nguyen et al., 2011). No experimental data and thermodynamic model could be found for the binary DEEA/MAPA and ternary of DEEA/MAPA/H_2O systems.

In this work, we report a set of new experimental data on the binary systems DEEA/H_2O and DEEA/MAPA as well as ternary VLE data for the DEEA/MAPA/H_2O system based on ebulliometer measurements. The gathered *P-T-x-y* data were modeled with a UNIQUAC thermodynamic model to determine the binary interaction parameters.

2. Experimental section

2.1. Material

Reagent grade 2-(diethylamino)-ethanol (DEEA) with purity $>>$ 99.5% and 3-(Methylamino)-propylamine (MAPA) with purity $>>$ 98.5% supplied by Sigma-Aldrich were used without further purification. The solutions were prepared gravimetrically by dissolving the chemicals in deionized water.

2.2. Vapor pressure measurements of pure DEEA(1) and pure MAPA (2)

The *P-T* vapor pressure data for pure solvents at different temperatures were measured in a modified Swietoslawski ebulliometer apparatus (Hartono et al., 2013; Kim et al., 2008). The measurements were started at ambient pressure to measure normal boiling point and then the pressure was reduced to generate data at lower temperatures.

2.3. Binary VLE measurements of the DEEA(1)+H_2O(3) and DEEA(1)+MAPA(2) systems

P-T-x-y data for the binary system DEEA/H_2O at different temperatures and concentrations were measured in the same apparatus. A gravimetrically prepared, 80 wt% solution of DEEA in water was initially fed to the ebulliometer. During the experiment, after each equilibration, the initial solution was diluted gradually to achieve high dilution at the end. While for MAPA/H_2O, the reported data (Kim et al., 2008) were collected and used.

P-T-*x-y* data of DEEA/MAPA system were also measured. By feeding pure DEEA or MAPA into the apparatus and diluting gradually with MAPA or DEEA to achieve high dilution at the end. The binary interaction parameters between the two amines could then be determined. This work was easy compared to the previous AMP/Pz system (Hartono et al., 2013), since both of the amines were in liquid state. Detailed experimental procedures can be found in previous work (Hartono et al., 2013; Kim et al., 2008).

2.4. Ternary VLE measurements of DEEA(1)+MAPA(2) +H_2O(3) system

Eight different concentrations of ternary DEEA/MAPA/H_2O solutions were prepared gravimetrically. They provided different mole ratios of DEEA/MAPA (0.20, 0.25, 0.40, 0.50, 2.0, 2.5, 4.0, and 5.0) and were individually fed into the ebulliometer. When equilibrium was established at a specific temperature, samples of liquid and vapor phase were collected. Each ratio of DEEA/MAPA was completed in one run from the lowest to the highest possible temperature.

2.5. Liquid (x) and vapor (y) phase analyses

The collected liquid and vapor solutions were examined with amine titration (Mettler Toledo G20) to determine the amine concentrations for the binary systems. High concentration samples were analyzed with 0.2 N H_2SO_4 as titrant but for the low concentration samples 0.02 N H_2SO_4 had to be used. The end point of each titration curve was used to calculate the concentration of amine according to Eq. (1).

For the binary DEEA/MAPA system, the concentration of each amine was estimated from the total alkalinity according to:

$$Alk\left(\frac{mol}{kg_{Solution}}\right) = \frac{2\cdot(M\cdot V)_{H_2SO_4}}{w_{sample}} \tag{1}$$

$$x_1 = \frac{(Alk\cdot M_2 - n_2)}{(n_1 - Alk\cdot M_1)}\cdot x_2 \tag{2}$$

$$x_1 + x_2 = 1 \tag{3}$$

For the ternary DEEA/MAPA/H_2O system, two parallel samples were analyzed with Liquid Chromatography-Mass Spectroscopy (LCMS) to quantify the concentration of each compound. The LC-MS analyzes were performed on an LC–MS/MS system, 6460 Triple Quadrupole Mass Spectrometer coupled with 1290 Infinity LC Chromatograph and Infinity Autosampler 1200 Series G4226A from the supplier Agilent Technologies. The same technique was implemented for different amines/alkanolamines and details regarding procedures can be found in previous works (Vevelstad et al., 2013; da Silva et al., 2012; Lepaumier et al., 2011). The reported concentrations were on volumetric base and to quantify each amine on the gravimetric basis the total alkalinities (*Alk*), (Eq. (1)) were measured by titration and the results from the LCMS were used as the mole ratio DEEA/MAPA (η). Hence the