Fluid Phase Equilibria 325 (2012) 90–99

Contents lists available at SciVerse ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Quantitative analysis of the liquid phase by FT-IR spectroscopy in the system CO_2/diethanolamine (DEA)/H_2O

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ARTICLE INFO

Article history:
Received 28 October 2011
Received in revised form 5 April 2012
Accepted 21 April 2012
Available online 30 April 2012

Keywords:
CO_2
DEA
Speciation
FT-IR
VLE
Henry constant

ABSTRACT

FT-IR spectroscopy was used to measure the liquid phase speciation in water–diethanolamine (DEA)–CO_2 system, the CO_2 loading varying from 0.04 to 0.9. The DEA mass fractions in the unloaded solution were 0.2, 0.3 and 0.4, and the temperature varied from 298.1 K to 333.1 K. The concentrations of carbamate and molecular CO_2 have been experimentally determined and the other species concentrations (DEA, protonated DEA, bicarbonate) have been deduced from mass balances and electroneutrality relation. These values, combined with the measurement of CO_2 partial pressure in equilibrium with the liquid phase, allow the determination of apparent CO_2 Henry constant $(H_{CO_2})_{DEAsolution}$ original values. These results show that $(H_{CO_2})_{DEAsolution}$ is independent of the CO_2 loading. Moreover, it is shown that the increase of temperature results in a decrease of $(H_{CO_2})_{DEAsolution}$.

1. Introduction

Aqueous alkanolamine solutions are widely used for the capture of acid gases found in natural gas or industrial flue gas. To design and optimize the process, an accurate reactive mass transfer model is required. For this purpose, representation of the liquid phase speciation through a realistic thermodynamic model is crucial for the evaluation of the driving forces as well as for the determination of a precise kinetic model all along the absorption column. Generally, the estimation of thermodynamic parameters is based on solubility data, *e.g.* the acid gas partial pressure as a function of the loading α (α is the acid gas mole number divided by the amine mole number). However, due to the complexity of the system with up to 9 species (in the case of primary or secondary amines), the database has to contain liquid phase speciation data to ensure a precise and reliable representation of the liquid phase.

For the last few years, many efforts have been made to obtain and publish such data. For instance, Benamor and Aroua have reported carbamate concentrations in CO_2 loaded diethanolamine (DEA) or methyldiethanolamine (MDEA) aqueous systems, using a titration method [1]. Nevertheless, the speciation determination is most often performed by spectroscopic methods. ^1H and ^{13}C NMR spectroscopy were the first analytical methods used to characterize the liquid phase. Thanks to ^1H or ^{13}C NMR measurements, Barth determined the ratio of the carbamate concentration to the concentration of carbonates and bicarbonates in aqueous solutions of diisopropanolamine (DIPA), DEA, monoethanolamine (MEA) and diglycolamine (DGA) [2]. The corresponding equilibrium constants related to the formation of carbamate were calculated. Suda et al. [3], Polpsteinova et al. [4], Böttinger et al. [5,6], Ermatchkov et al. [7] and Yang et al. [8] also used ^{13}C as well as ^1H NMR and observed different species: amine, protonated amine, bicarbonate, carbonate, carbamate and molecular CO_2. Quantitative results have been obtained, even though no difference can be made between the species that differ only by a proton (amine and protonated amine or carbonate and bicarbonate). Online analysis of the liquid phase was even achieved by Böttinger et al. [5,6] with a specifically designed experimental device.

Besides, in order to solve the issue of the quantification of the species which can not be distinguished by NMR spectroscopy, several authors turned to vibrationnal spectroscopy. Souchon et al. recently published speciation data determined by *in situ* Raman spectroscopy in the case of the H_2O/MDEA/CO_2 system. Carbamate stability constants for systems containing primary or secondary amines were also calculated from these measurements [9]. However, infrared spectroscopy is the most widely used vibrational spectroscopic method to determine the liquid phase composition of CO_2 loaded aqueous alkanolamine solutions. The first study was carried out by Rogers et al. [10,11]. In its experimental device, both the liquid and the gaseous phases were analyzed by FT-IR,

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http://dx.doi.org/10.1016/j.fluid.2012.04.016

but no clear exploitation of FT-IR spectra was presented. Lichtfers and Rumpf [12] have carried out experiments in order to make a speciation on the water–NH_3–CO_2 system by infrared spectrometry. Derks et al. have also determined the speciation in the system CO_2/MDEA/H_2O with a CaF_2 circulating cell [13] and considered the measurement of molecular CO_2 concentration as an objective for further development. Jackson et al. have built an apparatus allowing the *in situ* analysis of the liquid phase, using a diamond ATR probe but only qualitative results are reported [14].

Sidi-Boumedine [15] have developed the same kind of experimental set-up as Rogers et al. [10] in which an external loop allows the IR analysis of the liquid phase for DEA and MDEA loaded solutions using an ATR accessory. The peak corresponding to molecular CO_2 has been identified and the concentration of molecular CO_2 and the carbamate evolution have been determined. Using the same apparatus, Archane et al. [16] have published speciation data for the H_2O/DEA/Methanol/CO_2 system. These authors have also developed an original device using an ATR diamond accessory coupled to the FT-IR spectrometer in order to determine *in situ* the composition of the liquid phase together with VLE data. Similar speciation data were also published [17] (molecular CO_2 concentration and carbamate qualitative evolution) for the system H_2O/DEA/PEG400/CO_2.

In this study, the same apparatus as the one designed by Archane et al. [17] was used. IR spectral data have been treated in order to determine *in situ* the composition of the liquid phase in CO_2 loaded aqueous solutions of DEA together with VLE measurements.

VLE and liquid phase speciation measurements were performed at 298.1 K, 313.1 K and 333.1 K for DEA mass fractions ranging from 0.20 to 0.40. In the whole paper, the mass fraction of DEA, noted w_{DEA}, is relative to unloaded DEA/H_2O mixture. In order to increase the database used for thermodynamic modeling, VLE data were also acquired at 298.1 K for w_{DEA} fraction from 0.3 to 0.41. The aqueous solutions were loaded up to 0.9 mole CO_2 per mole of DEA.

2. Experimental

2.1. Experimental set-up

A detailed description of the experimental device is presented in the paper of Archane et al. [17]. The apparatus is presented in Fig. 1 and consists in a stainless steel double-jacketed cell ($V_{\text{cell}} = 294.2 \pm 0.1 \times 10^{-6}\,\text{m}^3$), equipped with a Pt100 temperature probe (precision ±0.1 K) and a pressure sensor (Drück PTX 611, 0–1000 kPa, ±1 kPa). The lid of the cell contains tubes and valves, for the introduction of the liquid and the gas. The temperature of the cell is monitored through the circulation of silicon oil in the double-jacket and the seal is overheated ($\Delta T = 3\,\text{K}$) to avoid any condensation phenomena. The liquid phase and the vapour phase are stirred by two four blades impellers. The bottom of the cell is drilled, and is fixed to an Attenuated Total Reflectance accessory (Durasample cell) put in the IR spectrometer (Bruker Tensor 27). It allows the *in situ* analysis of the liquid phase. As our aim is to determine the true concentration of all species, including molecular CO_2, interference with the atmospheric CO_2 has to be avoided. This is obtained by a circulation of CO_2- and water-free air inside the spectrometer.

2.2. Experimental procedure

CO_2 (Air Liquide, 99.995%) was used and water was freshly distilled prior to the preparation of amine aqueous solutions. DEA (Sigma Aldrich, 99%), $NaHCO_3$ (Sigma Aldrich, 99.5%) and aqueous hydrochloric acid (Sigma Aldrich, 36.5–38.0% mass) were used as received.

The solvents are individually degassed. For this purpose, water is freezed using liquid nitrogen and pumped under vacuum during 30 min, this procedure being repeated three times. DEA is heated at 323 K under vacuum during 5 h. The solutions are then prepared by weighing. The balance used in this work is the model XP 1203S, from Mettler Toledo. Typical weighed masses are 200 g for solvent (uncertainty = 0.001 g) and 1 g for gas (as the mass of the cylinder containing the CO_2 is about 900 g, the uncertainty associated to the gas measurement is 0.005 g).

At the beginning of each experiment, the cell is pumped under vacuum until a primary vacuum is obtained ($P < 1$ kPa). The solution containing DEA and water is then transferred inside the cell. When the target temperature T is reached, the pressure P_{vap}^{sat} corresponding to the solvent vapour pressure and the IR spectrum are both recorded. CO_2 is then introduced in the reactor. Its amount is measured by weighing the gas vessel before and after the addition. The pressure inside the cell and the IR spectrum are monitored and the equilibrium is supposed to be reached when no significant change is observed on both pressure and spectra within 1 h. After recording the spectrum and P_{tot}, a new addition of CO_2 is realized to get measurements at higher loadings.

2.3. CO_2 partial pressure and loading calculation

The CO_2 partial pressure P_{CO_2} is estimated from the measured total pressure P_{tot} by applying the Raoult's expression:

$$P_{CO_2} = P_{tot} - P_{vap}^{sat}(1 - x_{CO_2}^{app}) \tag{1}$$

where $x_{CO_2}^{app}$ is the apparent molar fraction of CO_2, which is the sum of the molar fraction of molecular carbon dioxide, carbamate ($DEACOO^-$), bicarbonate ($HCO_3{}^-$) and carbonates ($CO_3{}^{2-}$). In Eq. (1), the main part of P_{vap}^{sat} is the vapour pressure of water. Indeed, the vapour pressure of DEA varies from 0.05 Pa at 298.15 K to 2.43 Pa at 333.15 K [18] and DEA can be considered as a non volatile solvent. We have confirmed in a previous work [16] that Eq. (1) leads to a precise estimation of P_{CO_2} in a similar system. The difference between P_{CO_2} estimated from Eq. (1) and P_{CO2} measured by gas chromatography turned out to be less than 0.5%.

The loading α is defined as the ratio between the absorbed CO_2 mole number and the amine mole number in the liquid phase. According to Archane et al. assumptions and mass conservation considerations [16], α is expressed as follows:

$$\alpha = \frac{n_{CO_2,in} - [P_{CO_2}\varphi_{CO_2}^{vap}(V_{Cell} - V_{solution})/RT]}{n_{\text{DEA},in}} \tag{2}$$

where $n_{CO_2,in}$ is the total mole number of CO_2 introduced, $n_{\text{DEA},in}$ the DEA mole number introduced, V_{Cell} the volume of the cell, $V_{solution}$ the volume of the liquid phase, $\varphi_{CO_2}^{vap}$ the fugacity coefficient of CO_2 and R the ideal gas constant. $\varphi_{CO_2}^{vap}$ has been calculated using the virial equation of state: $\varphi_{CO_2}^{vap} = \exp(B/RT)$ with B the CO_2 virial second coefficient from van Huff [19]. The vapour phase correction implies a variation on the CO_2 loading less than 0.4%, considering $V_{\text{solution}}/V_{\text{vapour}} \approx 0.4$, where V_{vapour} is the volume of the vapour phase.

3. Quantitative analysis of the liquid phase

When CO_2 is added to an aqueous solution of DEA, the following equilibrium reactions take place:

$$\text{Amine protonation}: \quad DEA + H_3O^+ \leftrightarrow DEAH^+ + H_2O \tag{3}$$

$$\text{Carbon dioxide hydrolysis}: \quad CO_2 + H_2O \leftrightarrow HCO_3^- + H_3O^+ \tag{4}$$

$$\text{Bicarbonate hydrolysis}: \quad HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \tag{5}$$