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Determination of the liquid-phase speciation in the MDEA-H$_2$O-CO$_2$ system

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Abstract

Aqueous solutions of alkanolamines are commonly used in CO$_2$ capture processes. To describe these complex processes rigorous mass transfer models are needed, in which all mass transfer, kinetics and thermodynamics are incorporated correctly. To improve the quality of the thermodynamic models, not only commonly used P-α (CO$_2$ partial pressure versus CO$_2$ liquid loading) experimental data, but also liquid phase speciation data are important. Speciation data of amine-H$_2$O-CO$_2$ data are very scarce in literature. In this work speciation data of MDEA-H$_2$O-CO$_2$ have been determined experimentally with a Fourier Transform Infra-Red spectrometer (FTIR) at ambient temperature. After several calibration lines were prepared, the speciation of this system was determined online in the FTIR. The experimental data presented in this work were well in line with speciation from open literature.

1. Introduction

Alkanolamine solutions are commonly used in CO$_2$ regeneration processes. For the design and development of these processes, rigorous mass transfer models are required, to describe the compex chemical reactions which take place in the liquid phase. An important part of these mass transfer models are the thermodynamics models, which describe the physical and chemical equilibrium conditions. Until now, these thermodynamic models are regressed with so-called P-α experimental data in which the (total and or CO$_2$ partial) equilibrium pressure is measured as function of CO$_2$ liquid loading. However, also a detailed and correct liquid phase composition (not only total CO$_2$ concentrations) as a function of loading should be determined. This is because the speciation is required in the determination of the actual driving force for CO$_2$ absorption and desorption, and thus required input for the rigorous mass transfer modeling used in the design and operation of industrial gas treating equipment.

The fine-tuning and/or validation of the various (rigorous) thermodynamic models requires extensive data sets on the liquid phase speciation of solvents (partially) loaded with carbon dioxide. However, a literature survey on speciation data reveals that only in the past decade a reasonable number of studies on the liquid phase speciation in water –(alkanol)amine-carbon dioxide systems has been published in the open literature.
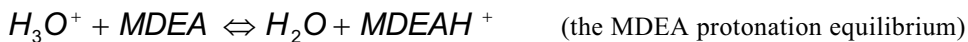
Typically, such speciation data were obtained using ^{1}H and/or ^{13}C NMR spectroscopy as described by e.g. Ermatchkov et al. [1], Poplsteinova-Jakobsen et al. [2] and Böttinger et al. [3], [4]. Using the NMR technique, quantitative information can be obtained on the concentration of amines, carbamates, bicarbonate and molecular CO_2. However, due to the fast proton transfer between molecular and protonated amines, only the sum of their concentrations can be obtained [1,3,4], unless an extensive calibration is performed [2]. The same applies to the carbonate and bicarbonate ion. Moreover, nuclear magnetic resonance can be a relatively laborious and time consuming analysis technique.

Sidi-Boumedine [5] used Fourier Transform Infra-Red (FTIR) spectroscopy to investigate the liquid-phase speciation in aqueous solutions of carbon dioxide and (alkanol)amines. His work demonstrated that FTIR spectroscopy allows for (quantitative and/or qualitative) analysis of individual components, such as e.g. molecular carbon dioxide, carbamate and bicarbonate.

In the present work, a technique was developed for the quantitative analysis of the liquid phase composition of (aqueous) solutions of carbon dioxide and (alkanol)amine solutions, which is based on FTIR spectroscopy as well. The method was validated with speciation measurements on the system containing carbon dioxide, water and N-methyldiethanolamine (MDEA).

2. Main objectives and experimental technique

When carbon dioxide is dissolved in e.g. an aqueous MDEA solution, the following equilibrium reactions take place, leading to a total of eight different species in the liquid:

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$ (the water dissociation equilibrium)

$$2H_2O + CO_2 \Leftrightarrow H_3O^+ + HCO_3^-$$ (the bicarbonate formation equilibrium)

$$H_2O + HCO_3^- \Leftrightarrow H_3O^+ + CO_3^{2-}$$ (the carbonate formation equilibrium)

$$H_3O^+ + MDEA \Leftrightarrow H_2O + MDEAH^+$$ (the MDEA protonation equilibrium)

The 'complete speciation' of this system can be obtained by combining experimental techniques. Relatively simple experimental methods on the speciation include the measurement of the pH and the conductivity of a solution at equilibrium; the pH provides information on the (activity of) H_3O^+ and/or the OH^- ion, while the conductivity is a measure for the sum of ionic species present in the solution. Subsequently, it was demonstrated by Sidi-Boumedine [5] that FTIR spectroscopy can be applied to quantify the amounts of the bicarbonate ion and molecular carbon dioxide. Information on the MDEA protonation equilibrium would further reduce the number of unknowns in the system, and the focus of this study was, therefore, to develop a method which allows for the individual, quantitative determination of molecular and protonated MDEA.

2.1. FTIR specifications

All samples were measured using a Varian 670-IR with a gas-bearing interferometer with a resolution of 4 cm^{-1}, over a range of 4000 – 400 cm^{-1} and an attenuator with a selected intensity of 25 %. All spectra were created (as the

average) from 16 scans. The window material used in the on-line liquid flowcell (Specac Ltd. London, UK) was calciumfluoride (CaF_2) and a spacer of approx. 30 μm was used to create the desired path length. The samples were introduced to the infrared beam via this liquid flow cell using a reciprocal pump (FMI, NY, USA). Data from the IR-spectrometer were processed using a PC with Varian Resolution Pro software (Varian Australia). Spectra were analysed using Peakfit from Seasolve, Framingham, USA.

2.2. Sample preparation

The test samples of CO_2 in MDEA solution were obtained in a (thermostatted) vigorously stirred reactor connected to a calibrated gas vessel, both equipped with temperature and pressure indicators. Also, a vacuum pump was connected to the reactor, to remove all inert gases from the setup and dissolved gases from the amine solutions before the preparation of the sample. A schematic overview of the experimental set-up is presented in Figure 1.
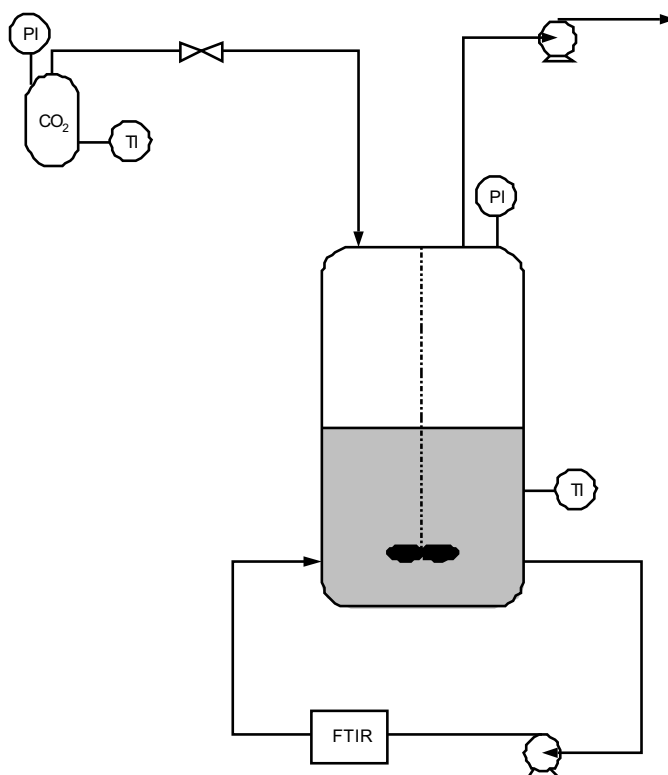

Figure 1. Experimental set-up used in this work.

In a typical experiment, an aqueous solution of freshly prepared N-methyldiethanolamine (purity 99 %, Acros Organics) of known composition was transferred to the reactor vessel. Next, the liquid was degassed by applying vacuum for a short while and allowed to reach its vapor pressure at the desired temperature and consecutively the (vapor) pressure was recorded. Subsequently, the gas supply vessel was filled with pure carbon dioxide (quality 4.8, Air Liquide) and the initial pressure and temperature in this vessel were measured. Next, the valve between the gas supply vessel and the reactor was opened and a sufficient amount of CO_2 was allowed to reach the reactor, after which the valve was closed again.

Next, the reactor stirrer was switched on and the contents of the reactor were allowed to reach equilibrium, which was reached when the reactor pressure remained constant. The equilibrium CO_2 partial pressure was derived from this final (equilibrium) reactor pressure corrected for the vapor pressure of the lean solution. The initial and final pressure and temperature in the gas vessel were used to calculate the corresponding CO_2 loading of the solution. Next, a sample from the liquid phase was transferred by means of a pump into the flow cell of the FTIR apparatus.

Using the procedure described above, one integrated experimental solubility data point is obtained which provides information not only on the equilibrium carbon dioxide partial pressure but also on the liquid phase speciation at the desired conditions with respect to (alkanol)amine concentration, carbon dioxide loading and temperature.

3. Results and discussion

An inhouse, calibration method was developed prior to the quantitative analysis of the samples containing aqueous solutions of carbon dioxide and N-methyldiethanolamine. Individual calibration curves were constructed for the components MDEA (molecular MDEA, protonated MDEA and the bicarbonate ion), in which the amplitude of the absorbance peak – at a certain wavenumber – is given as a function of the concentration of the respective component. A typically obtained FTIR spectrum is given in Figure 2, while results of initial, calibration experiments are displayed in Figure 3:
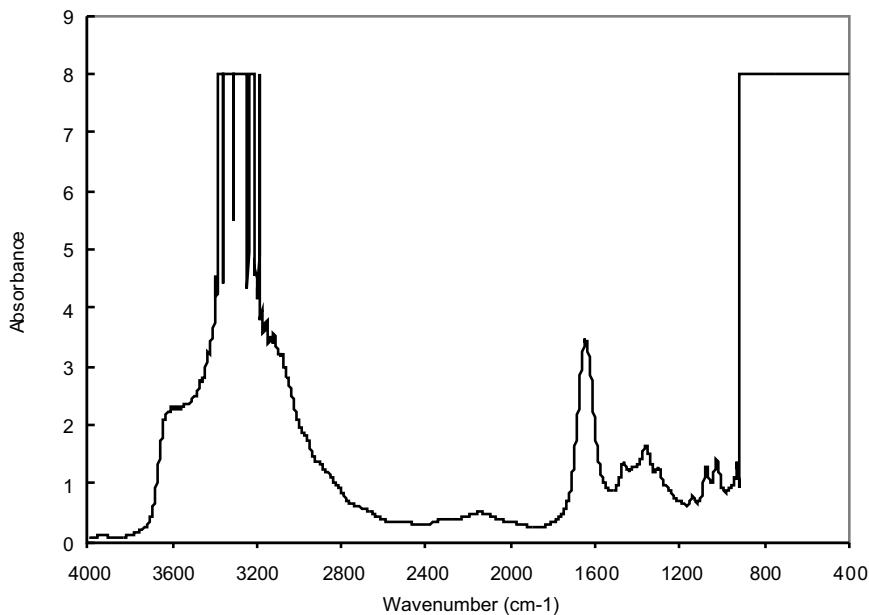

Figure 2. A typical spectrum obtained during an FTIR analysis of a CO_2 – MDEA – H_2O sample.
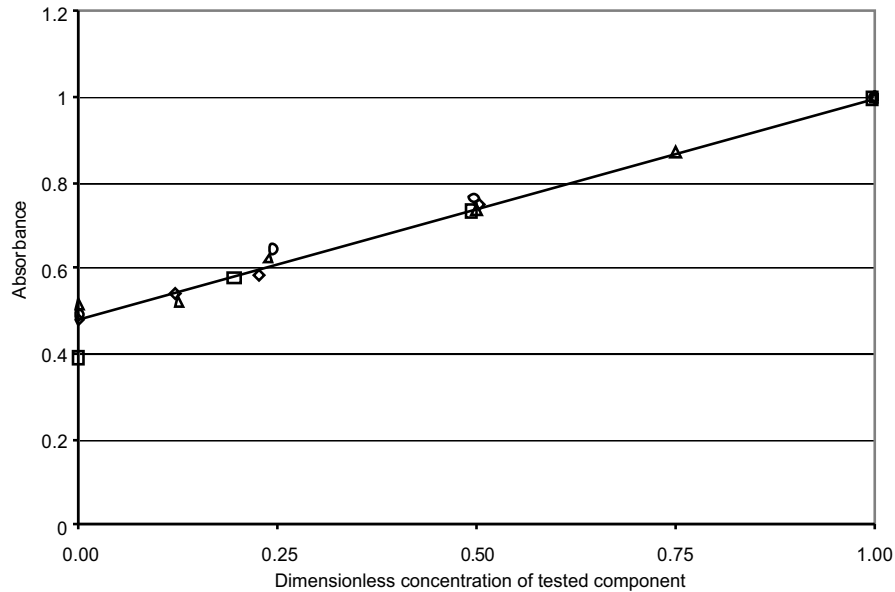
Figure 3. Typical experimental result of an FTIR analysis. The different symbols represent different series of experiments of the same component.

From the results shown in Figure 3, two conclusions can be drawn :

- The results obtained with the current configuration (FTIR & flow cell) are repeatable ;
- There is a clear, linear relation between the absorbance and the concentration of the investigated component; in other words: the system obeys the Lambert-Beer law at the conditions studied.

Upon completion of the calibration curves, the absorbance spectra of the "MDEA-H_2O-CO_2" samples were recorded and interpreted. The results are listed in Table 1, and, in Figure 3, a graphical comparison is made between the newly obtained experimental data and the speciation data reported by Poplsteinova-Jakobson.

Table 1. Liquid phase speciation results in an aqueous 2 kmol m^{-3} MDEA solution loaded with carbon dioxide at room temperature.

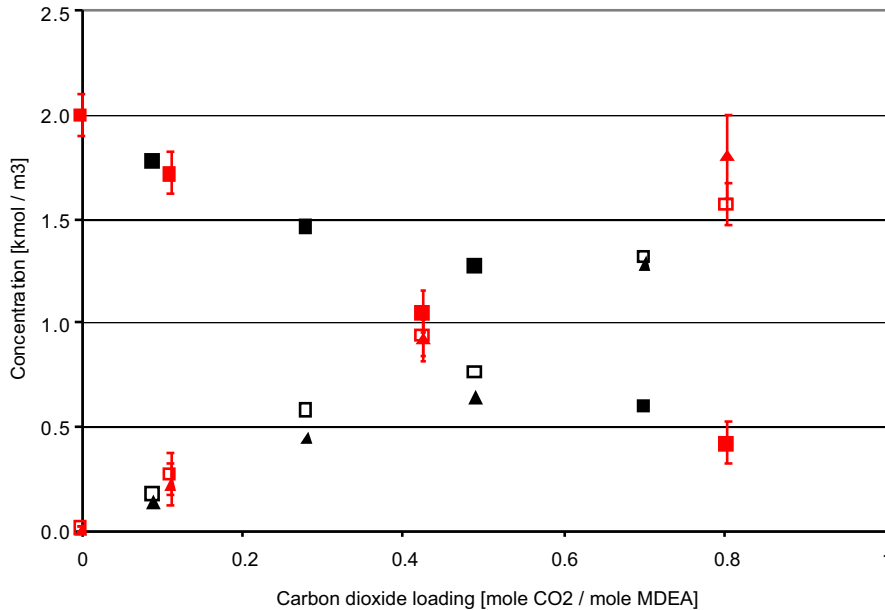| Loading [mol CO_2 / mol MDEA]	C_{MDEA} [kmol m^{-3}]	C_{MDEAH+} [kmol m^{-3}]	C_{HCO3-} [kmol m^{-3}]
0	2.00 ± 0.1	0.02 ± 0.0	0.0 ± 0.0
0.11	1.72 ± 0.1	0.28 ± 0.1	0.22 ± 0.1
0.42	1.05 ± 0.1	0.95 ± 0.1	0.92 ± 0.1
0.80	0.43 ± 0.2	1.57 ± 0.1	1.80 ± 0.2

Figure 4. Liquid phase speciation results in an aqueous 2 kmol m^{-3} MDEA solution loaded with carbon dioxide at room temperature. Comparison of the present data (red) with Poplsteinova-Jakobsen et al. [2] (black). ■ ■ = MDEA ; □□ = MDEAH$^+$; ▲▲ = HCO$_3^-$.

From Figure 4, it can be concluded that the results obtained with the newly developed liquid speciation analysis technique using a FTIR are well in line with the NMR data reported in the open literature regarding the studied components : molecular MDEA ; protonated MDEA and the bicarbonate ion.

Further development of the FTIR technique will include the following steps :

- The quantitative analysis of the components (molecular) carbon dioxide and the carbonate ion ;
- Analysis of the liquid phase speciation of aqueous carbon dioxide - MDEA solutions at higher temperatures (up to about 125 °C), thereby covering both absorber and desorber conditions ;
- The analysis of the liquid phase composition of aqueous solutions of carbon dioxide and primary/secondary alkanolamines (such as e.g. monoethanolamine), thereby also including the carbamate species.
- The experimental setup is to be extended with both a pH and a conductivity electrode.

4. Acknowledgements

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