In situ determination of species distribution in alkanolamine-H$_2$O-CO$_2$ systems by Raman spectroscopy

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Abstract

Most of the CO$_2$ post-combustion capture units under development for fossil-fuel based power plants rely on the use of alkanolamine aqueous solutions. The correct design of absorbing and regenerating sections of these processes require robust thermodynamic and kinetic models. This legitimates current research efforts in the field of the characterization of aqueous alkanolamine loaded solutions. In this study, the potentialities of Raman spectroscopy are investigated. The obtention of species distribution for MDEA loaded solutions at 40°C is described. Numerical adjustments of thermodynamic parameters from spectral measurements for MEA and DEA is also performed. Compared to other classical analytical tools, a strong interest is shown for the analysis of tertiary amines solutions and potentially for kinetic measurements.

Keywords: CCS; CO$_2$; alkanolamine solutions; Raman spectroscopy; species distribution

1. Introduction

Carbon dioxide (CO$_2$) is nowadays considered as one of the main greenhouse gases and is officially associated with climate change and global warming. In order to reduce CO$_2$ emissions, CO$_2$ capture and storage (CCS) is recognized as a key climate change mitigation technology. More specifically, this includes the development of cost-efficient post-combustion processes that capture CO$_2$ from the flue gas of fossil-fuel based power plants or strongly emitting industries (refineries, steel or cement works). Most of these post-combustion processes rely on the use of aqueous solutions of alkanolamines as sorbents for carbon dioxide. Accurate determination of the thermodynamic properties of these systems is of major interest for both fundamental and economical considerations, since the design of CO$_2$ absorption columns strongly depends on thermodynamic models (also called vapor-liquid equilibrium -VLE- models). Whatever the VLE model used, it requires the optimisation of parameters which can account for the composition of the liquid phase. Until recently, these parameters were generally determined by numerical adjustment from CO$_2$ equilibrium partial pressure measurements in the gas phase, without any consideration for the species distribution in the liquid phase.

It is only in the last decade that surveys on the composition of the liquid phase have been carried out. $^1$H NMR and more especially quantitative $^{13}$C NMR were described as efficient tools for the study of species distribution in CO$_2$ loaded alkanolamine solutions. Indeed, experimental results allow to understand reaction mechanisms but...
also provide quantitative information that can be used to measure chemical equilibrium constants or thermodynamic parameters. Böttiger et al. have even recently reported online measurements by NMR spectroscopy thanks to a specifically designed apparatus. However, in situ measurements are not easily performed and acquisition times for quantitative $^{13}$C NMR experiments (typically 8 hours for one experiment) are unsuited for kinetic experiments.

In order to overcome these problems, vibrational spectroscopy has also been considered. FT-IR spectroscopy only allows the qualitative monitoring of a few species. Regarding Raman spectroscopy, it is a powerful tool for quantitative analysis for concentrations in the range of 0.1 to 100 %. It is relatively fast, sensitive, suitable for measurements in aqueous media because of the weak Raman scattering efficiency of water molecules, and easy-to-handle for in situ analysis thanks to fiber optics and immersion probes. Despite these advantages, only a few studies have been reported: on H$_2$O-CO$_2$ systems, aqueous alkali metal bicarbonate and carbonate solutions, ammonium carbonate, bicarbonate and carbamate equilibria, or conformational studies on DMAE (2-(N,N-dimethylamino)ethanol) or MAE (2-(N-methylamino)ethanol) solutions with CO$_2$. In the present work, we propose a new method using Raman spectroscopy for the quantitative determination of the species distribution in alkanolamine-H$_2$O-CO$_2$ systems. Raman spectra of CO$_2$ loaded alkanolamine aqueous solutions (monoethanolamine MEA, diethanolamine DEA and N-methylethanolamine MDEA) are recorded in situ at equilibrium at 40°C. A vigorously stirred thermostated cell under CO$_2$ pressure and a Raman immersion probe are employed. Concentrations of free amine, protonated amine, bicarbonate and carbonate anions are determined for MDEA aqueous solutions. In parallel, equilibrium constants for the carbamate formation reaction are fitted from spectral data obtained on MEA and DEA CO$_2$ loaded aqueous solutions. Comparisons of the experimental results with a thermodynamic model and literature data are presented and discussed.

2. Experimental section

Carbon dioxide was purchased from Air Liquide (99.995 %) and $^{13}$C-labeled CO$_2$ from Cortecnet, Inc. Monoethanolamine (MEA, 99 %), diethanolamine (DEA, 99 %), N-methylethanolamine (MDEA, 99 %), were purchased from Sigma-Aldrich and degassed before use. Aqueous solutions of amines were freshly prepared with degassed Millipore water. HCl 32 % (Aldrich), sodium hydrogen carbonate NaHCO$_3$ and sodium carbonate Na$_2$CO$_3$ were of analytical grade (Merck).

Reference solutions of protonated amines were prepared from amine solutions by addition of 1.1 equivalent of HCl. Reference solutions of CO$_2^{2-}$ and HCO$_3^-$ were freshly prepared by dissolution of their corresponding sodium salt in Millipore water. Because HCO$_3^-$ is amphoteric, a 10 % decomposition rate of HCO$_3^-$ into CO$_3^{2-}$ and H$_2$CO$_3$ at 40°C was considered.

A dedicated apparatus was designed to conduct the online Raman spectroscopic investigations. It allows the acquisition of vapor-liquid equilibrium data as well as the Raman spectra of loaded alkanolamine aqueous solutions. It consists in a thermostated cell equipped with an immersion probe coupled with a Raman spectrometer. Solutions are prepared from degassed liquids, weighted and introduced in the reactor. Their density is measured with a vibrating tube densimeter (DMA 4100, Anton Paar). In order to remove ambient air from the cell, the solvent is rapidly degassed at room temperature until the pressure stabilizes to equilibrium saturation vapor pressure. The solution is heated to the desired temperature and carbon dioxide is added stepwise from a bomb under vigorous agitation. Stabilization of the pressure in the cell typically occurs within 10 to 20 minutes. Raman spectra of the liquid phase are then acquired at low stirring rate (50 rpm) between each addition. Knowing the pressure, temperature and volume of the bomb, the amount of CO$_2$ inside the bomb is evaluated using PV/T data. Thus, the injected amount of gas is obtained from the pressure drop in the bomb following each injection. The pressures of the cell and of the gas reservoir are monitored with calibrated LEX1 and LEO3 digital manometers (Keller, Switzerland) respectively. Temperatures are measured with type K thermocouples. From the well-known total volume of the cell, the amount of carbon dioxide in the gas phase is obtained. The loading of liquid phase $\alpha$ is deduced from mass conservation equations. $\alpha$ is defined as the ratio between dissolved carbon dioxide and total amine concentration whatever their chemical forms.

All the Raman spectra were acquired at 40°C with a RXN2C spectrometer (Kaiser Optical Systems Inc.) equipped with a quarter-inch immersion probe made of Hastelloy C276. The excitation beam is delivered by a 785 nm Invictus laser. Spectra were recorded in the range 100-3425 cm$^{-1}$ with a resolution of 1.5 cm$^{-1}$. The acquisition time was set to 60 s which allows a satisfactory signal to noise ratio. The spectra of aqueous solutions were...
systematically corrected by subtracting the contribution of water which is considered to be equal to the spectrum of pure water weighted by the water content of the solution. Then, they were divided by the corresponding initial amine concentration. The Raman spectra of reference compounds were recorded at 40°C, manually baseline-corrected when needed and divided by their concentration expressed in mol.L⁻¹.

¹³C NMR data were acquired at 40°C with a 300 MHz spectrometer (Bruker) on ¹³C-labelled CO₂ loaded MDEA solutions in H₂O/D₂O 1:1. Chemical shifts were measured with TSP-d₄ as internal reference and its chemical shift was set to -2.35 ppm. A calibration curve relating the chemical shift of the HCO₃⁻/CO₃²⁻ peak to the molar fraction of the two species was obtained from the NMR spectra of standard weighted solutions of NaHCO₃ and Na₂CO₃ in H₂O/D₂O 1:1.

3. Thermodynamic model description

The model used in this work is an activity coefficient approach to the excess Gibbs free energy. It is based on chemical equilibria in the liquid phase. In the system CO₂-alkanolamine-H₂O, the involved chemical reactions are the following:

Dissociation of water: \[ 2H₂O \leftrightarrow HO^- + H₃O^+ \] (I)
Hydrolysis of carbon dioxide: \[ CO₂ + 2H₂O \leftrightarrow H₂CO₃^- + H₃O^+ \] (II)
Dissociation of bicarbonate anion: \[ H₂CO₃^- + H₂O \leftrightarrow CO₃²⁻ + H₅O^+ \] (III)
Dissociation of alkanolamine: \[ R₁R₂R₃NH^+ + H₂O \leftrightarrow R₁R₂R₃N + H₃O^+ \] (IV)

Primary and secondary amines are also known to react directly with CO₂ to form stable carbamates:

Carbamate formation except tertiary amines: \[ R₁R₂R₃NCOO^- + H₂O \leftrightarrow K \rightarrow R₁R₂R₃NH + HCO₃^- \] (V)

where \( R₁R₂R₃N \) is the chemical formula of the alkanolamine. \( R_i \) represents either an alkyl group, an alkanol group or a hydrogen atom.

Equilibrium constants for reactions (I)-(IV) are available in the literature in molality units. For the carbamate formation, \( K \) represents the chemical reaction equilibrium constant of equation (V).

The water content of the liquid phase is assumed not to vary with the chemical reactions. To determine the composition of the liquid phase, a system of 8 equations is solved: 5 mass action laws corresponding to each chemical reaction, 2 mass balances equations which are related to amine and carbon dioxide respectively and finally the electroneutrality equation. Approximations are made in this work: the activity coefficient of water is taken equal to its mole fraction and the activity coefficients of molecular solutes (amine, free acid gas carbon dioxide) are set to unity. Finally, the activities of the ionic species are given by the extended Pitzer Debye-Hückel equation:

\[ \log[\gamma] = \frac{-A\sqrt{I}}{1 + BrI} + CI \] (I)

where \( A \) and \( B \) are two constants which represent the solvent and depend only on temperature, \( r \) is the closer approach diameter, \( C \) is an empirical parameter and \( I \) is the ionic strength defined as:

\[ I = \frac{1}{2} \sum_j m_j z_j^2 \] (2)

where \( z_j \) is the charge number on the ion and \( m_j \) its molality.

4. Results and discussions

Raman spectra of loaded solutions were recorded at 40°C for CO₂ partial pressure up to 3 bar. This temperature is representative of experimental conditions in the absorbing section of acid gas removing units. The amine solutions investigated are 5, 20, 40 wt% MEA, 10, 20, 40 wt% DEA and 10, 23.5, 40 wt% MDEA.
4.1. Qualitative description of Raman spectra

The evolution of the corrected Raman spectra is presented on Figure 1. Experimental VLE data are in good agreement with thermodynamic models, suggesting that thermodynamic equilibrium is reached when acquiring Raman spectra. Whatever the type of amine considered, the reaction with CO₂ leads to important spectral changes. They are related to the progressive protonation of the amine and the formation of ionic species (HCO₃⁻, CO₃²⁻ and carbamates with primary or secondary amines).

![Figure 1: Raman spectra with varying CO₂ loading at 40°C for (a) 20 wt% MEA, (b) 20 wt% DEA and (c) 23.5 wt% MDEA. Blue lines stand for unloaded amine solutions spectra.](image)

Reference spectra of HCO₃⁻, CO₃²⁻, amines and their protonated forms are given in Figure 2. They correspond to the spectra that would be recorded at 40°C for 1 mol.L⁻¹ aqueous solutions and to which the contribution of water is subtracted. Such reference spectra for carbamate species are not available because they cannot be isolated in water. At the loadings considered in this study, molecular carbon dioxide is generally not observed in the aqueous alkanolamine solutions (vibrational bands at 1383 and 1279 cm⁻¹). Its contribution to the Raman spectrum can thus be neglected because of its low concentration. Upon addition of carbon dioxide, protonation of amines leads to a shift to higher wavenumbers of alkane C-H stretching vibrations in the region 2800-3000 cm⁻¹ [21]. The whole footprint (300-1500 cm⁻¹) of the amines Raman spectra is also affected and characteristic peaks of protonated amines are easily recognizable. Along with these changes in amine vibrations, characteristic peaks of hydrogen carbonate anion HCO₃⁻ appear: at 1015 cm⁻¹ (C-OH stretch), 1360 cm⁻¹ (symmetric stretch) with a shoulder at 1300 cm⁻¹ (C-OH bend), 670 cm⁻¹ and 630 cm⁻¹ (HO-CO bend). Although the CO₃²⁻ symmetric stretching vibration
band at 1065 cm\(^{-1}\) is very sharp, its contribution to the total Raman signal is barely visible because of CO\(_3^{2-}\) low concentration.

For MEA loaded solutions, peaks at 580 and 1162 cm\(^{-1}\) are clearly identified as carbamate vibrational bands since they cannot be attributed to any other scattering species in the mixture. Moreover, their intensity increases from \(\alpha = 0\) to \(\alpha = 0.5\) and then decreases. Regarding DEA, identification of characteristic Raman vibrational bands is less obvious. Except for a peak at 1160 cm\(^{-1}\), other vibrations are hidden under the Raman signal of other species. On the other hand, as a tertiary amine, MDEA does not form carbamates. All the spectral evolution can be assigned to varying concentrations of MDEA, MDEA-H\(^+\), HCO\(_3^-\) and CO\(_3^{2-}\).

4.2. Quantitative analysis of Raman data

In this study, Raman spectra of loaded alkanolamine aqueous solutions are considered to be linear combinations of pure compounds spectra. It is a classical hypothesis in Raman spectroscopy. Only minor deviations are observed for highly concentrated MDEA solutions (40 wt\% and in lesser extent 23.5 wt\%). In which cases, it was noted that the HCO\(_3^-\) spectrum is slightly modified. These changes consist in a slight band broadening effect for the 1015 cm\(^{-1}\) band and in the increase of the relative intensity of the C-OH bending vibration at 1300 cm\(^{-1}\) compared to the stretching vibration at 1360 cm\(^{-1}\).

![Figure 3](image-url) Speciation diagram obtained from Raman data (markers) or modelled (lines) at 40°C for (a) 23.5 wt\% MDEA and (b) 40 wt\% MDEA aqueous solutions.

4.2.1. Tertiary amines

On the basis of pure component spectra of amines, protonated amines, bicarbonates (HCO\(_3^-\)) and carbonates (CO\(_3^{2-}\)), quantitative analysis for tertiary amines loaded solutions such as MDEA is achieved using the DCLS (Direct Classical Least Squares) algorithm. Experimental spectra are decomposed with reference spectra or reference peak areas with a least squares approach. First of all, the spectral zone between 2700 and 3100 cm\(^{-1}\) is analysed with the amine and its acidic form as reference areas and their respective concentrations are determined. The concentrations of bicarbonate and carbonate anions are then deduced from the residual spectral area in the 965-1055 cm\(^{-1}\) and the 1055-1075 cm\(^{-1}\) regions. The experimental error is evaluated by checking total alkanolamine concentration and electroneutrality. As expected, total MDEA concentration, expressed in mol.L\(^{-1}\), is nearly constant. Total excess charge never exceeds 6 \% of the initial concentration of amine. While neglecting the concentration of molecular CO\(_2\), the CO\(_2\) loading, \(\alpha\), is estimated from speciation data as the ratio between HCO\(_3^-\) and CO\(_3^{2-}\) concentrations and the total amine concentration. A good agreement is observed between these values and
the CO₂ loadings resulting from mass balance measurements. The absolute average error for \( \alpha \) is only 0.02. A maximum value of 0.07 is obtained for 10 wt\%. MDEA solutions at \( \alpha = 1.01 \) It corresponds to experimental conditions where molecular CO₂ cannot be neglected any more and should be included in the calculation of the overall loading.

In Figure 3, the calculated speciations (markers) and their comparison with modelled concentrations (lines) are reported for MDEA 23.5 wt\% and 40 wt\% at 40°C as a function of the measured CO₂ loading. In the 23.5 wt\% case, no major differences are noted between Raman data and the thermodynamic model. In the 40 wt\% case, some considerable discrepancies appear: the protonated amine is systematically overestimated by the model whereas the free amine is underestimated. The most striking difference with the thermodynamic model or other published models is the significantly smaller concentration of carbonate anion determined by Raman spectroscopy.\(^{[8]}\) It can nevertheless be considered as reliable since CO₃\(^{2-}\) symmetric stretching band efficiency is particularly high. Indeed, modelled concentrations would lead to more intense spectral changes around 1065 cm\(^{-1}\). As a consequence, Raman spectra analysis tends to prove that modelled speciation is certainly biased for high concentrations. This gap between VLE model in the liquid phase and Raman data may be an explanation for the deviations observed for the modelling of CO₂ absorption isotherm data which are known to be increasing with the total amine weight ratio.

In order to check Raman speciation calculations, \(^{13}\)C NMR experiments were also carried out according to the previously described procedure. NMR spectroscopy does not distinguish an amine species from its protonated form because of the fast exchange of protons. However, the chemical shift of the HCO\(_3^-\)/CO\(_3^{2-}\) peak strongly depends on the ratio of the two species. As shown on Figure 4, a linear calibration for the chemical shift versus the molar fraction of CO\(_3^{2-}\) can be obtained in an aqueous medium.

Upon addition of \(^{13}\)CO₂ in a 40 wt\%. MDEA aqueous solution in H\(_2\)O/D\(_2\)O 1:1, the chemical shift of this peak continuously decreases from 160.9 ppm to 160.4 ppm (\( \alpha = 0.82 \)). By comparison with the calibration curve, it suggests that the proportion of HCO\(_3^-\) is logically increasing but it also raises the question of the validity of this calibration curve in a real medium. Some of the measured chemical shifts are indeed lower than the one for pure HCO\(_3^-\) standard solution. At most, it can be concluded that HCO\(_3^-\) predominates in MDEA loaded solutions but obtaining quantitative information remains tricky due to non negligible matrix effects. Consequently, Raman spectroscopy turns out to be an unique and efficient tool for the study of tertiary amines aqueous solutions.

\[ y = -20.981 + 0.13039x \quad R = 0.99991 \]

\( \frac{[\text{CO}_3^{2-}] / ([\text{HCO}_3^-] + [\text{CO}_3^{2-}])}{} \)

**Figure 4:** Molar fraction of CO\(_3^{2-}\) versus HCO\(_3^-\)/CO\(_3^{2-}\) chemical shift at 40°C.

### 4.2.2. Primary and secondary amines

Pure component spectra are not available for carbamate species of primary and secondary amines. Thus, concentration profiles cannot be directly obtained by DCLS. Spectral measurements can nevertheless be used for fitting thermodynamic models using non-linear least-squares regression. Indeed, these mathematic methods are widely used to fitting of thermodynamic or kinetic models. It is applicable to any multivariate data that show a linear relationship between signal and concentration (Beer-Lambert's law).\(^{[22,23]}\) Especially, it allows the simultaneous
determination of non-linear parameters (such as equilibrium constants of the thermodynamic model) as well as pure component spectra for spectroscopically active species. Among the non-linear parameters of the VLE model described here, carbamate stability constant $K_c$ is certainly the most interesting floating parameter to be fitted since its value greatly influences the species distribution. Thus, Raman data at 40°C for MEA and DEA loaded solutions were analysed and carbamate stability constants $K_c$ were calculated. The algorithm leading to $K_c$ determination for a primary or secondary amine is the following. First, Raman spectra are arranged in a data matrix $A$ that is assumed to be a linear combination of the concentrations $C$ and the reference spectral responses $V$ of the $n$ predominant chemical components (amine, protonated amine, HCO$_3^-$, CO$_3^{2-}$ and carbamate). $E$ is a matrix error:

$$A = CV + E = CV = \sum_{i=1}^{n} c_i v_i = \sum_{i\neq carb} c_i v_i + c_{carb} v_{carb}$$  \hspace{1cm} (3)$$

For a given trial value of $K_c$, trial concentration matrix is calculated from total amine concentration, CO$_2$ loading and temperature for each experiment with the help of the previously described thermodynamic model. All the reference spectra $v$ are known experimentally except for carbamate species ($\hat{v}_{carb}$). This system of linear equations has an explicit least-squares solution for $\hat{v}_{carb}$. The best estimate value for $\hat{v}_{carb}$ is given by the following equations:

$$\hat{v}_{carb} = C^+ Y$$ \hspace{1cm} (4)

with:

$$C^+ = (\hat{c}_{carb} \hat{c}_{carb})^{-1} \hat{c}_{carb} \hat{c}_{carb}$$ \hspace{1cm} (5)

and

$$Y = A - \sum_{i\neq carb} \hat{c}_i v_i$$ \hspace{1cm} (6)

For each fit and each value of $K_c$, the elements of a residual matrix $\hat{R}$ and an objective function $ssq$ equal to the sum of its square coefficients can be determined:

$$\hat{R} = A - \sum_{i\neq carb} \hat{c}_i v_i - \hat{c}_{carb} \hat{v}_{carb}$$ \hspace{1cm} (7)

$$ssq = \sum_{i=1}^{n_{exp}} \sum_{j=1}^{n_w} (r_{ij})^2$$ \hspace{1cm} (8)

with $n_{exp}$ the number of experiments simultaneously fitted and $n_w$ the number of wavenumbers considered.

The values of $K_c$ are determined for each amine to minimize $ssq$ according to a modified Levenberg-Marquardt algorithm. The investigated spectral area was chosen to be 900-1400 cm$^{-1}$ because it includes characteristic vibration bands of both HCO$_3^-$ and MEA or DEA carbamate species. This is of major importance since $K_c$ substantially influences the ratio of these two species. The optimisation results for MEA and DEA and their comparison with published data are reported in Figure 5 as well as the optimized spectral responses for carbamates.

<table>
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<tr>
<th>Values of pKc = -log $K_c$</th>
<th>This work</th>
<th>Chan et al.$^{[24]}$</th>
<th>Aroua et al.$^{[25]}$</th>
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<tbody>
<tr>
<td>MEA</td>
<td>1.4 ± 0.3</td>
<td>1.27</td>
<td>-</td>
</tr>
<tr>
<td>DEA</td>
<td>0.63 ± 0.3</td>
<td>0.43</td>
<td>0.59</td>
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</table>

Figure 5: (left) Fitted values of pKc (= - log $K_c$) with $K_c$ expressed in molality units at 40°C and (right) corresponding fitted Raman spectra of carbamate species.
The fitted values for the $K_c$ equilibrium constants are in accordance with literature data. This result tends to validate the Raman methodology described here. Hence, it may be considered for fitting thermodynamic parameters such as $K_c$ for unknown primary or secondary amines. However, it must be kept in mind that this method can only determine thermodynamic parameters that significantly affect the species distribution. Adjusting secondary parameters such as $r$ or $C$ in the model is certainly too daring considering the accuracy of the method.

5. Conclusions

The use of Raman spectroscopy is shown to be a very promising technique for the quantitative analysis of the liquid phase of CO$_2$-loaded alkanolamines aqueous solutions. Particularly, the species distribution for tertiary amines like MDEA is obtained from spectral measurements. Comparatively, Raman spectroscopy proves to be more efficient than NMR spectroscopy in these cases. Concerning primary and secondary amines such as MEA and DEA, the carbamate formation equilibrium constant at 40°C can be calculated within the frame of a given thermodynamic model. Even if such a performance can be achieved by quantitative $^1$H or $^{13}$C NMR with a better accuracy and a simpler data treatment, Raman spectroscopy acquisition times are much smaller. Therefore, it can be considered as a highly efficient tool for the improvement of both thermodynamic and kinetic models.

Reference List