Estimating species concentration in CO$_2$-loaded monoethanolamine using Raman spectroscopy

Ahmad Syukri Na’im Bin Mohd Hanafiah$^1$, Abdulhalim Shah Maulud$^1,2$
$^1$Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610, Perak, Malaysia.
$^2$Centre of Contaminant Control & Utilization, Institute of Contaminant Management, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610, Perak, Malaysia.

ahmad_0009857@utp.edu.my, halims@utp.edu.my

Abstract. Operation of amine plant for CO$_2$ removal had long been plagued with inefficiencies due to suboptimal operating parameter leading to losses in operational expenditure. Improving the system requires understanding into thermodynamics and kinetics of the process which can be made possible through having information on the qualitative and quantitative speciation in the alkanolamine system. In this work, potential of Raman spectroscopy as a monitoring tool for species concentration in CO$_2$-loaded aqueous monoethanolamine (MEA) system was investigated. CO$_2$ loading data from experimental work were used with Kent Eisenberg model to estimate species concentrations (dissolved CO$_2$, Protonated amine, Bicarbonate, Carbonate, Carbamate and unreacted MEA). Each species concentration were fitted to experimentally-acquired Raman spectrum using Partial Least Squares Regression (PLSR) technique to develop calibration model. Evaluation of regression plots, $R^2$ and Root Mean Square Error (RMSE) shows good predictive accuracy compared to the thermodynamically-predicted species concentration.

Keyword: Raman spectroscopy, carbon dioxide, MEA, PLS, Kent Eisenberg

1. Introduction

Carbon Dioxide (CO$_2$) had been an environmental issue globally due to its role as the main greenhouse gas that leads to global warming as well as climate change. In natural gas production industry, CO$_2$ is a known corrosive agent in the pipeline that also reduce the Gross Heating Value of the gas, lowering sale price per volume. Aqueous amine solvents for chemical absorption of CO$_2$ (amine–CO$_2$–H$_2$O systems) are considered to be a robust separation technology to remove carbon dioxide (CO$_2$) due to its operational flexibility and technology maturity as well as absorption rate and capacity compared to other CO$_2$ removal technology (1). Monoethanolamine (MEA), a primary amine, is among the widely used amine class in the industry due to the high reaction rate with CO$_2$ in comparison with other amine classes.

Increasing the efficiency of an amine process requires establishing overview on the thermodynamics and kinetics of the system through understanding the species present and their interspecies interaction. Raman spectroscopy is an analytical technique which is applicable for quantitative analysis of chemical species in a phase. The technique had previously been utilized to quantify phase equilibria, transport properties and species’ concentration in liquid and gas sample (2).

Interpreting the spectrum from Raman spectra requires development of calibration model specific for the chemical species of interest. Kent Eisenberg thermodynamic model is among the technique available for predicting speciation in CO$_2$-loaded amine. The model simplified the iterative calculation required by lumping non-idealities into the equilibrium constant that are fitted to experimental data resulting in a relatively good predictive capabilities. Kent-Eisenberg model is capable to estimate species concentration in CO$_2$-loaded system.
concentration with good accuracy over a wide-range of CO2 loading, between 0.2 to 0.8 mol of CO2 per mol of amine (3).

In this work, Raman spectroscopy will be used in conjunction with Kent-Eisenberg model and PLSR technique to develop a set of calibration models that is capable to predict the species concentration in CO2-loaded aqueous MEA solution at 4 and 5 molar concentration. An experimental setup with the capabilities to collect vapor-liquid equilibrium data and Raman spectra of the CO2-loaded aqueous MEA system simultaneously was constructed. Species concentrations are estimated using Modified Kent Eisenberg model and CO2 concentration is calculated using Henry’s Law. Finally, Raman calibration models are developed from preprocessed Raman spectra and the species concentration using PLSR technique. The performance of each models are determined by evaluating their coefficient of determination (R2) and Root Mean Square Error (RMSE).

2. Materials and Experimental Method

2.1 Materials
Minimum Carbon dioxide gases with 99% purity was procured from Linde Malaysia Sdn. Bhd. MEA was sourced from Merck Sdn. Bhd. with purity >99%. Aqueous solution of MEA with concentration of 4 and 5 molar was prepared by dilution with deionized water. The MEA solution was prepared gravimetrically using laboratory scale.

2.2 Experimental setup and method
The experimental setup consists of a single feed vessel connected to a reaction vessel, in which both are equipped with pressure and temperature sensor as well as temperature controller. Raman spectroscopy unit is procured from StellarNet. The unit uses laser source with power of 500W and wavelength of 785 nm. The resolution of the unit is 4 cm⁻¹ with signal to noise ratio of 1000:1. A probe connected to the Raman unit was mounted to the reaction vessel to collect Raman spectrum. The data on CO2 loading were iteratively calculated using pressure drop method up to 20 bar pressure inside reaction vessel that was set at constant temperature of 303.15 K. By measuring PVT data from feed vessel, the amount of injected CO2 is quantified from the pressure drop inside the vessel after an injection. The amount of CO2 in gas phase is calculated based on PVT data together with the overall volume of reaction vessel and the CO2 loading was calculated using equation (1):

\[ \alpha = \frac{\left(\frac{PV}{g2009 + g4680 + g3023 + g3255 + g3271 + g4678}{g3265 + g3284 + g3275 + g3281 + g3435 + g3271 + g3267 + g3271 + g3127 + g3271 + g3276}} \right)}{RTn_{amine}} \]  

(1)

Where V is volume, P is pressure, Z is compressibility factor, R is general gas constant, T is temperature and n is number of moles of CO2 gas. i and f denotes the initial and final state representing before and after the CO2 gas is transferred into the reaction vessel. Peng-Robinson equation of state was used to quantify Z. Raman spectra were captured as the system reached equilibrium. 67 and 71 number of spectra was captured for 4 and 5 molar aqueous MEA solution respectively.

Thermodynamic Framework
Kent Eisenberg model was used to estimate the species concentration for aqueous MEA system at equilibrium condition (4). Aqueous MEA reaction with CO2 follows acid-base reaction and produced numerous ions as described in the reaction equations (2)-(6):

\[ AlkH^+ \leftrightarrow Alk + H^+; \ K_1 \]  

(2)

\[ AlkCOO^- + H_2O \leftrightarrow Alk + HCO_3^-; \ K_2 \]  

(3)

\[ CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-; \ K_3 \]  

(4)
The value for equilibrium constants $k_3 (4.38 \times 10^{-7})$, $k_4 (1 \times 10^{-14})$ and $k_5 (4.65 \times 10^{-11})$ were available from literature (5). The value of $k_1$ and $k_2$ were treated as fitting parameter for experimental data. Three balance equation of (7) – (9) were also considered in order to calculate the unknown species concentration.

Amine balance:

$$[\text{Alk}_{\text{total}}] = [\text{Alk}] + [\text{AlkH}^+] + [\text{AlkCOO}^-]$$  \hspace{1cm} (7)

CO$_2$ balance:

$$a[\text{Alk}_{\text{total}}] = [\text{HCO}_3^-] + [\text{AlkCOO}^-] + [\text{CO}_2^2^-] + [\text{CO}_2]$$  \hspace{1cm} (8)

Electroneutrality balance:

$$[\text{AlkH}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + [\text{AlkCOO}^-] + 2[\text{CO}_2^2^-]$$  \hspace{1cm} (9)

Henry’s law was applied to quantify the concentration of carbon dioxide dissolved in liquid phase:

$$[\text{CO}_2] = \frac{n_{\text{CO}_2}}{n_{\text{CO}_2}}$$  \hspace{1cm} (10)

The polynomial form of the model that was derived from equation (2) – (9) is described below:

$$A[H^+]^5 + B[H^+]^4 + C[H^+]^3 + D[H^+]^2 + E[H^+] + F = 0$$  \hspace{1cm} (11)

Where:

$$A = 1$$
$$D = -\frac{[\text{Alk}_{\text{total}}][k_{p3}^m][\text{CO}_2]}{k_2} - k_1^m k_5 - k_1^m k_3[\text{CO}_2] - 2k_3 k_4[\text{CO}_2]$$
$$B = [\text{Alk}_{\text{total}}] + k_1^m$$
$$E = \frac{k_1^m k_2 [\text{CO}_2]}{k_2} - \frac{k_1^m k_2^2 [\text{CO}_2]^2}{k_2} - 2k_3^m k_4 [\text{CO}_2]$$
$$C = -k_5 - k_3^m [\text{CO}_2] + \frac{k_3^m [\text{CO}_2]^2}{k_2}$$
$$F = -2k_3^m k_4 [\text{CO}_2]^2$$

The model was fitted with experimental loading data so that accurate calculation of species concentration is acquired. The defined $k_1^m$ serve as adjustable parameter to improve prediction accuracy of the model towards the experiment parameters. (6–8). Parameter $k_1^m$ is defined below:

$$k_1^m = k_1 f$$  \hspace{1cm} (12)

As for $f$:

$$f = q \ln \left( P_{\text{CO}_2} \right) + r \ln (\text{Alk}_{\text{total}})$$  \hspace{1cm} (13)

Using the defined framework, hydrogen ion concentration were calculated. Value considered were between $10^{-7}$ and $10^{-12}$ consistent with the pH values in the solution between 7 and 12 (3). Using the hydrogen ion concentration and equilibrium constants values, species concentration were calculated from the balance equations.
2.3 Calibration models development and evaluation
Baseline correction was performed on each Raman spectrum followed by smoothening using Savitsky-Golay method to reduce noise while preserving information contained in characteristic peaks within the spectrum. Raman calibration models were developed using preprocessed Raman spectra and species concentration by applying Partial Least Square Regression (PLSR) technique. The datasets were randomly segregated into calibration and validation datasets. Models were developed from calibration datasets using PLSREGRESS function in MATLAB. The technique develops regression model between important predictor variables and response variable by least square concept. \( \text{(9)} \). Scree plot was utilized to estimate the optimum number of PLS components \( \text{(10)} \). Coefficient of Determination \( \text{(R}^2 \text{)} \) and Root Mean Square Error (RMSE) for calibration and validation data were determined during model development to provide overview on the developed model and assess the regression performance.

3. Results and discussion
Comparison of Raman spectra between unloaded and CO\(_2\)-loaded MEA at 4 and 5 molar concentration were conducted. In figure 1, the peaks were observed to form at range between 800 cm\(^{-1}\) and 1100cm\(^{-1}\) as well as 1250 cm\(^{-1}\) and 1400 cm\(^{-1}\) due to changes in species composition caused by CO\(_2\) absorption into the solution and chemical reactions between species as described in equation (2) to (6). Among the ionic species present includes Protonated amine, Bicarbonate, Carbonate and Carbamate as well as unreacted MEA and dissolved CO\(_2\). Characteristic bands contains the peak that formed due to the inelastic Raman scattering as the results of collision between ions or molecules with laser source. The characteristic bands are unique for each chemical species in the CO\(_2\)-loaded MEA system.

![Figure 1](image1.png)

**Figure 1.** Raman spectrum of Unloaded and Loaded aqueous MEA at 4 molar concentration.

The characteristic band for a particular chemical species contains variables that are highly correlated with a particular chemical species. The variables contributed highly towards explaining the variance of the model for the species correlated with it. The contribution were reflected in the PLS weight plot from bicarbonate at 4 molar MEA concentration in figure 2. The peaks appeared between 500 and 1500 cm\(^{-1}\) indicating the variables within that range are highly correlated to the response variables and contribute the most towards the variance in the model. This is reflective to the literature finding where characteristic band for bicarbonate is located at 1017 cm\(^{-1}\). Other peaks are from weak intensity signals at 632 cm\(^{-1}\), 1360 cm\(^{-1}\) and 1630 cm\(^{-1}\) due to (OH)CO band, symmetric CO stretching and anti-symmetric CO\(_2\) stretch respectively \( \text{(8,11–14)} \).

![Figure 2](image2.png)

**Figure 2.** Weight Plots from bicarbonate calibration model (4M MEA) for PLS Component 1.
Coefficient of determination ($R^2$) and root mean square error for calibration (RMSEC) and validation (RMSEV) datasets were determined. These parameters evaluate the quality of the model in providing prediction value for species concentration compared to measured values. The values are presented in table 1.

| Species/CO$_2$ Loading | Amine concentration (mol/L) | R$_2$ Calibration | R$_2$ Validation | RMSEC | RMSEV |
|------------------------|-----------------------------|-------------------|------------------|-------|-------|
| CO$_2$                 | 4                           | 0.9438            | 0.9075           | 0.0771| 0.0790|
|                        | 5                           | 0.9562            | 0.9092           | 0.0652| 0.0758|
| MEAH-                  | 4                           | 0.9400            | 0.9031           | 0.2653| 0.3564|
|                        | 5                           | 0.9460            | 0.9137           | 0.3256| 0.3655|
| HCO$_3^-$              | 4                           | 0.9421            | 0.9027           | 0.2727| 0.3407|
|                        | 5                           | 0.9485            | 0.9039           | 0.3181| 0.4228|
| CO$_3^{2-}$            | 4                           | 0.9361            | 0.9031           | 0.0027| 0.0035|
|                        | 5                           | 0.9321            | 0.9254           | 0.0052| 0.0059|
| MEA                    | 4                           | 0.9304            | 0.9074           | 0.2820| 0.3163|
|                        | 5                           | 0.9211            | 0.9017           | 0.3736| 0.3963|
| MEACOO$^-$             | 4                           | 0.9497            | 0.9082           | 0.0364| 0.0518|
|                        | 5                           | 0.9282            | 0.9003           | 0.0565| 0.0661|
| CO$_2$                 | 4                           | 0.9358            | 0.9147           | 0.0439| 0.0580|
|                        | 5                           | 0.9311            | 0.9050           | 0.0497| 0.0460|

It was observed that for 4 molar aqueous MEA solution, the $R^2$ values for calibration models are above 0.90. The average $R^2$ calibration value is 0.9397 while for validation is 0.9067. As for 5 molar aqueous MEA solution, the $R^2$ values for calibration models are also above 0.90 with average values of 0.9376 for calibration and 0.9085 for validation respectively. The results were indicative that the developed PLSR calibration models are capable of predicting MEA concentration with good accuracy. The performance were supported by the observation of regression plots. Examples of the plots were displayed in figure 3 for bicarbonate, carbamate and unreacted CO$_2$ in 4 molar MEA solution. It was observed that the data points were well distributed along the regression line for all models which indicates good fit between the data and the model. Small deviation was observed between actual and predicted data points which was reflected by the resulting RMSEC and RMSEV value.

![Figure 3](image-url)

It was also noted that during the development of calibration model, the whole spectrum range was utilized. However, the characteristic band for a chemical species are present only at specific spectral range within a Raman spectrum based on literature. Other variables outside the spectral range are considered as noises. Developing calibration models by utilizing specific spectral range that was...
correlated with the particular species could enhance the signal by reducing noises that interfere during model development thus improving the model performance (15,16).

4. Conclusion
The potential of Raman spectroscopy as a monitoring tool for species concentration in CO₂-loaded aqueous monoethanolamine (MEA) system were investigated. The R² values from the developed calibration models were above 0.90 from calibration and validation datasets while the RMSE values improved throughout model optimization. The regression plots show close data distribution along the regression line. The result signifies that the models are capable to predict species concentration with good accuracy in CO₂-loaded aqueous MEA system.

5. References
[1] Puxty G, Maeder M. The fundamentals of post-combustion capture. Absorption-Based Post-Combustion Capture of Carbon Dioxide, 2016, p. 13–33. doi:10.1016/B978-0-08-100514-9.00002-0.
[2] Smith E, Dent G. Modern Raman Spectroscopy - A Practical Approach. 2005. doi:10.1002/0470011831.
[3] Suleman H, Maulud AS, Man Z. Review and selection criteria of classical thermodynamic models for acid gas absorption in aqueous alkanolamines. Rev Chem Eng 2015;31:599–639. doi:10.1515/revce-2015-0030.
[4] Kent RL, Eilsenberg B. BETTER DATA FOR AMINE TREATING. Hydrocarb Process 1976.
[5] Edwards TJ, Maurer G, Newman J, Prausnitz JM. Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes. AIChE J 1978. doi:10.1002/aic.690240605.
[6] Aroua MK, Salleh RM. Solubility of CO₂ in aqueous piperazine and its modeling using the Kent-Eisenberg approach. Chem Eng Technol 2004;27:65–70. doi:10.1002/ceat.200401852.
[7] Haji-Sulaiman MZ, Aroua MK, Benamor A. Analysis of equilibrium data of CO₂ in aqueous solutions of DEA, MDEA and their mixtures using the modified Kent Eisenberg Model. Trans IChemE 1998;76:1–8. doi:10.1205/026387698525603.
[8] Wong MK, Bustam MA, Shariff AM. Chemical speciation of CO₂ absorption in aqueous monoethanolamine investigated by in situ Raman spectroscopy. Int J Greenh Gas Control 2015;39:139–47. doi:10.1016/j.ijggc.2015.05.016.
[9] Wold S, Jöström M, Eriksson L. PLS-regression: A basic tool of chemometrics. Chemom. Intell. Lab. Syst., 2001. doi:10.1016/S0169-7439(01)00155-1.
[10] Varmuza K, Filzmoser P. Introduction to Multivariate Statistical Analysis in Chemometrics. 2009. doi:10.1366/000370210791114185.
[11] Kachko A, van der Ham L V., Bardow A, Vlugt TJH, Goetheer ELV. Comparison of Raman, NIR, and ATR FTIR spectroscopy as analytical tools for in-line monitoring of CO₂ concentration in an amine gas treating process. Int J Greenh Gas Control 2016;47:17–24. doi:10.1016/j.ijggc.2016.01.020.
[12] Souchon V, Alexio MDO, Delpoux O, Sagnard C, Mougin P, Wender A, et al. In situ determination of species distribution in alkanolamine- H₂O - CO₂ systems by Raman spectroscopy. Energy Procedia 2011;4:554–61. doi:10.1016/j.egypro.2011.01.088.
[13] Carvalho LAEB De. Raman spectra, conformational stability and normal coordinate analysis of ethylmethylamine 1995;26. doi:10.1002/jrs.1250260811.
[14] Larkin P. IR and Raman Spectra-Structure Correlations. Infrared Raman Spectrosc., 2011. doi:10.1016/B978-0-12-386984-5.10006-0.
[15] Axrup L, Markides K, Nilsson T. Using miniature diode array NIR spectrometers for analysing wood chips and bark samples in motion. J. Chemom., 2000. doi:10.1002/1099-128X(200009/12)14:5/6<561::AID-CHEM608>3.0.CO;2-2.
[16] Xu F, Wang D. Rapid determination of sugar content in corn stover hydrolysates using near infrared spectroscopy. Bioreour Technol 2013. doi:10.1016/j.biortech.2013.08.071.
6. **Acknowledgments**
Authors wished to acknowledge PETRONAS Research Sdn. Bhd. and Universiti Teknologi PETRONAS for the financial assistance and supports for undertaking this research work.