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Estimating species concentration in CO₂-loaded monoethanolamine using Raman spectroscopy

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Abstract. Operation of amine plant for CO₂ 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 CO₂-loaded aqueous monoethanolamine (MEA) system was investigated. CO₂ loading data from experimental work were used with Kent Eisenberg model to estimate species concentrations (dissolved CO₂, Protonated amine, Bicarbonate, Carbonate, Carbamate and unreacted MEA). Each species concentration were fitted to experimentally-acquired Raman spectrum using Partial Least Square Regression (PLSR) technique to develop calibration model. Evaluation of regression plots, R₂ 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 (CO₂) 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, CO₂ 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 CO₂ (amine–CO₂–H₂O systems) are considered to be a robust separation technology to remove carbon dioxide (CO₂) due to its operational flexibility and technology maturity as well as absorption rate and capacity compared to other CO₂ 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 CO₂ 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 CO₂-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 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

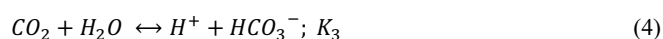
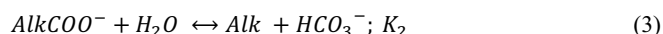
The experimental setup consists of a single feed vessel connected to a reaction vessel, in which both are equipped with pressure and temperature sensor as well as temperature controller. Raman spectroscopy unit is procured from StellarNet. The unit uses laser source with power of 500W and wavelength 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):

$$\alpha = \frac{\left[V_{FV} \left(\frac{P_i}{Z_i} - \frac{P_f}{Z_f} \right) - \left(\frac{P_{RV}(V_{RV} - V_{amine})}{Z_{RV}} \right) \right]}{RTn_{amine}} \quad (1)$$

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):





The value for equilibrium constants k_3 (4.38×10^{-7}), k_4 (1×10^{-14}) and k_5 (4.65×10^{-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:

$$[Alk_{total}] = [Alk] + [AlkH^+] + [AlkCOO^-] \quad (7)$$

CO₂ balance:

$$\alpha[Alk_{total}] = [HCO_3^-] + [AlkCOO^-] + [CO_3^{2-}] + [CO_2] \quad (8)$$

Electroneutrality balance:

$$[AlkH^+] + [H^+] = [OH^-] + [HCO_3^-] + [AlkCOO^-] + 2[CO_3^{2-}] \quad (9)$$

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

$$[CO_2] = \frac{P_{CO_2}}{H_{CO_2}} \quad (10)$$

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

$$A[H^+]^5 + B[H^+]^4 + C[H^+]^3 + D[H^+]^2 + E[H^+] + F = 0 \quad (11)$$

Where:

$$\begin{aligned} A &= 1 & D &= -\frac{[Alk_{total}]k_1^m k_3 [CO_2]}{k_2} - k_1^m k_5 - k_1^m k_3 [CO_2] - 2k_3 k_4 [CO_2] \\ B &= [Alk_{total}] + k_1^m & E &= -\frac{k_1^m k_3 k_5 [CO_2]}{k_2} - \frac{k_1^m k_3^2 [CO_2]^2}{k_2} - 2k_1^m k_3 k_4 [CO_2] \\ C &= -k_5 - k_3 [CO_2] + \frac{k_1^m k_3 [CO_2]}{k_2} & F &= -\frac{2k_1^m k_3^2 k_4 [CO_2]^2}{k_2} \end{aligned}$$

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:

$$k_1^m = k_1 f \quad (12)$$

As for f :

$$f = q \ln(P_{CO_2}) + r \ln(Alk_{total}) \quad (13)$$

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. (9). Scree plot was utilized to estimate the optimum number of PLS components (10). Coefficient of Determination (R^2) 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 1100 cm^{-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.

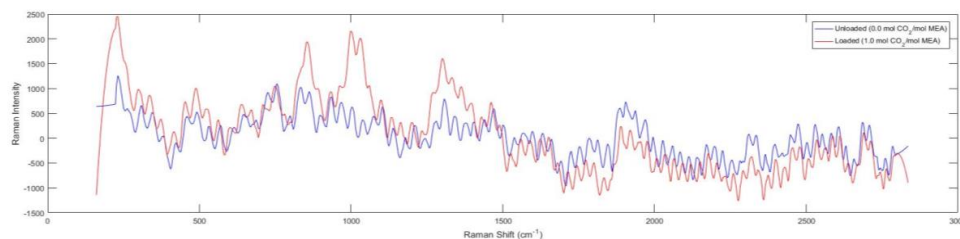


Figure 1. Raman spectrum of Unloaded and Loaded aqueous MEA at 4 molar concentration.

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 $(\text{OH})\text{CO}$ band, symmetric CO stretching and anti-symmetric CO_2 stretch respectively (8,11–14).

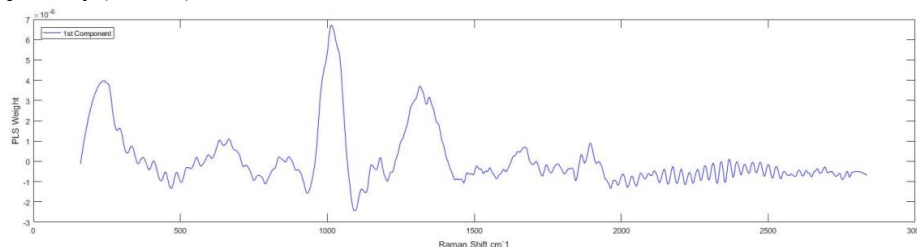


Figure 2. Weight Plots from bicarbonate calibration model (4M MEA) for PLS Component 1.

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.

Table 1. Performance evaluation results for calibration models.

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
Loading	5	0.9562	0.9092	0.0652	0.0758
MEA ⁺	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 CO₂ 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.

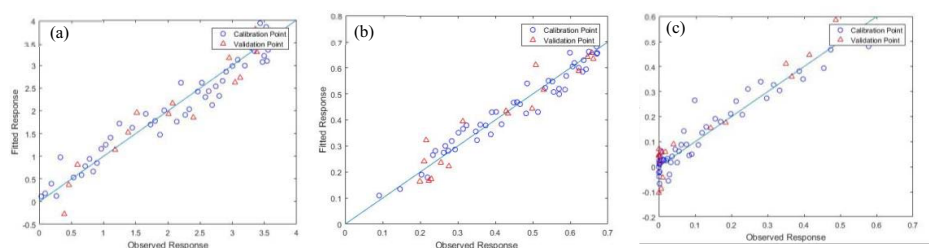


Figure 3. Regression plots from 4M MEA calibration models. (a) Bicarbonate (b) Carbamate (g) Unreacted CO₂.

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 shows 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.

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6. Acknowledgments

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