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Speciation of MEA-CO₂ adducts at equilibrium using Raman spectroscopy

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Abstract

Among a number of initiatives proposed for capturing CO₂, the post-combustion technology is attractive as it offers fewer problems to be dealt with and does not require massive reconstruction of the existing power plants, thus reducing the economic penalty. In this paper, we present new vapor liquid equilibrium data for the solubility of CO₂ in MEA at 30, 40 and 50 wt% at a temperature of 40 °C. The data are compared with establish data obtained from literature and showed a close agreement. The ability of Raman spectroscopy to quantify the species present during the reaction is explored in this paper. First, calibration plots of carbonate, bicarbonate and carbamate are constructed based on the Raman active bands at 1065 cm⁻¹, 1019 cm⁻¹ and 1034 cm⁻¹, respectively. A detailed analysis of the species present during the reaction of aqueous MEA and CO₂ using Raman spectroscopy is discussed in this paper.

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1. Introduction

In industry, chemical absorption using aqueous amines such as ethanolamine (MEA) and methyl diethanolamine (MDEA) have been utilized to capture CO₂ after complete combustion of the fuels.[1] These amines are chosen based on several factors such as high reactivity, net cyclic capacity, tendency to form carbamates and bicarbonates,

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cost of regeneration and corrosiveness. There is a continuous effort among researchers in the field to find and characterize new and better CO₂ absorbents.[2, 3] One such activity is equilibrium measurements.

In a typical laboratory experiment, a new possible solvent is evaluated by measuring the partial pressure of CO₂ across a range of loadings (moles of CO₂/moles of solvent). The experimental setup usually consists of an equilibrium cell connected to an instrument able to quantify CO₂ partial pressures. The CO₂-loaded solvent was kept at a fixed temperature to attain equilibrium before measurement is performed. Liquid samples were then withdrawn from the sampling compartment for loading analysis. This procedure is laborious and some inconsistencies are observed in reported literature data. A reliable online or semi online method of determining liquid species present would greatly alleviate the workload. Earlier, we demonstrated the applicability of Raman spectroscopy in determining scattering factor of relevant bands by utilizing standard perchlorate solution.[4] In this paper, we present new vapor liquid equilibrium data for MEA at different concentrations and partial pressures with more in-depth analysis of the liquid phase species leading to more information being extracted from each experiment. We also performed uncertainty analysis to accurately quantify our experimental data, and evaluated our findings with the vast amount of equilibrium data available for MEA in literature.

2. Experimental section

2.1. Materials

All the chemicals were purchased from suppliers as shown in Table 1 and used without any purification. A Mettler Toledo balance (uncertainty ± 0.001 g) was used to weigh the required amount of MEA needed. Aqueous solutions of MEA were prepared using degassed deionized water (conductivity, 18.2 M Ω cm).

Table 1. Details of the chemicals used during experiments. N/A: Not available

Chemical	Purity (mass %)	Supplier
Ethanolamine (MEA)	≥ 99.5	Merck KGaA
Hydrochloric acid (HCl)	N/A	Merck KGaA
Sodium hydroxide (NaOH)	N/A	Merck KGaA
Barium chloride dehydrate (BaCl ₂ ·2H ₂ O)	N/A	Merck KGaA
Sodium carbonate (Na ₂ CO ₃)	≥ 99.5	Merck KGaA
Sodium bicarbonate (NaHCO ₃)	≥ 99.7	Merck KGaA
Ammonium carbamate	≥ 98.0	Alfa Aesar

2.2. CO₂ solubility experiments

A schematic diagram of the equilibrium cell used for measuring CO₂ solubility in MEA is shown in Fig. 1. A detailed description of the system was reported in our previous publications.[5, 6] In a typical experiment, only one bottle was filled with aqueous MEA solution and temperatures in the liquid and gas phases were monitored and controlled using temperature controllers supplied from WEST Control Solutions. Equilibrium was assumed to have been achieved when the total pressure and temperatures in liquid and gas phases remains unchanged over a period of 2 hours. At least six gas samples were collected and analyzed using gas chromatograph at each CO₂-loading, and a liquid sample was withdrawn and analyzed using BaCl₂ method as discussed in these publications.[6-8]

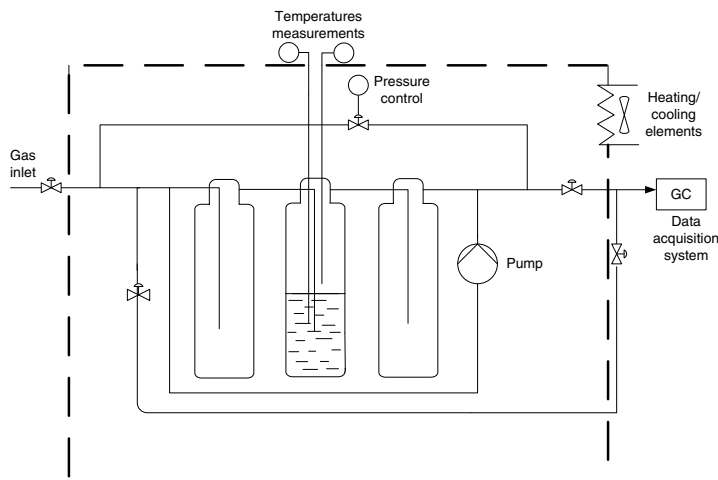


Fig. 1. Equilibrium cell flowsheet.

2.3. Raman spectroscopy experiments

At least 20 reference solutions of carbonate, bicarbonate and carbamate were freshly prepared using degassed MilliQ water. All the Raman spectra were acquired at 40 °C with a RXN2 spectrometer supplied by Kaiser Optical Systems Inc. An immersion probe which delivers a 400 nm laser beam was used to collect the spectra of reference solutions and of the CO₂-loaded amine solutions. The acquisition time was set at 60 s to allow a satisfactory signal to noise ratio. The spectra were also corrected by subtracting the contribution of water.

2.4. Uncertainty analysis

Uncertainty analyses were performed for gas and liquid phase samples as discussed in our earlier publications.[5, 6] Equation 1 shows factors that were included in the uncertainty calculation for gas phase samples. The uncertainty due to the total pressure during experiments $u(P)$ is 0.011 bar while the uncertainty due to temperature change $u(T)$ is 0.115 °C. The uncertainty due to our instrument calibration can be obtained from daily calibration measurements and normally this value is very small since the level of confidence for our calibration plots is very high.

$$u_c^2(P_{\text{CO}_2}) = (P_{\text{CO}_2})^2 \left[(\text{rep})^2 + \left(\frac{u(P)}{P} \right)^2 + \left(\frac{u(T)}{T} \right)^2 + \left(\frac{u(A)}{A} \right)^2 \right] \quad (1)$$

Equation 2 illustrates the factors considered in the calculation of combined uncertainty of the liquid phase samples: repeatability of titration experiments (rep), mass of sample (m), concentration of amine (C), volumes of HCl (V_{HCl}) and NaOH (V_{NaOH}) consumed during experiments. To take into consideration the contribution from analysis of a blank sample, uncertainties due to volumes of HCl and NaOH consumed during titration is multiplied by 2. The values of standard deviation were used to quantify the repeatability factor for our experimental samples.

$$u_c^2(\alpha_{\text{CO}_2}) = (\alpha_{\text{CO}_2})^2 \left[(\text{rep})^2 + \left(\frac{u(m)}{m} \right)^2 + \left(\frac{u(C)}{C} \right)^2 + 2 \left(\frac{u(V_{\text{HCl}})}{V_{\text{HCl}}} \right)^2 + 2 \left(\frac{u(V_{\text{NaOH}})}{V_{\text{NaOH}}} \right)^2 \right] \quad (2)$$

3. Results and Discussion

3.1. VLE data for MEA at different concentrations

The vapor liquid equilibrium data for CO₂ in aqueous solution of MEA with uncertainties is presented in Table 2. Experiments were performed at three different concentrations of 30, 40 and 50 wt% at a temperature of 40 °C.

Table 2. Equilibrium solubility of CO₂ in aqueous solution of MEA at 40 °C.

30 wt%		40 wt%		50 wt%	
α_{CO_2}	p_{CO_2}	α_{CO_2}	p_{CO_2}	α_{CO_2}	p_{CO_2}
0.242 ± 0.005	0.021 ± 0.009	0.173 ± 0.005	0.0343 ± 0.010	0.178 ± 0.043	0.0063 ± 0.003
0.321 ± 0.006	0.038 ± 0.008	0.242 ± 0.007	0.0405 ± 0.012	0.213 ± 0.021	0.0108 ± 0.006
0.330 ± 0.007	0.043 ± 0.006	0.306 ± 0.015	0.0510 ± 0.025	0.235 ± 0.007	0.0129 ± 0.005
0.345 ± 0.016	0.050 ± 0.014	0.344 ± 0.020	0.0765 ± 0.024	0.289 ± 0.016	0.0238 ± 0.011
0.352 ± 0.010	0.064 ± 0.029	0.394 ± 0.055	0.0918 ± 0.048	0.338 ± 0.037	0.0444 ± 0.113
0.355 ± 0.010	0.097 ± 0.025	0.427 ± 0.029	0.1725 ± 0.034	0.397 ± 0.064	0.1642 ± 0.036
0.375 ± 0.019	0.107 ± 0.028	0.449 ± 0.044	0.3432 ± 0.026	0.425 ± 0.023	0.4106 ± 0.029
0.377 ± 0.027	0.123 ± 0.060	0.468 ± 0.027	0.7496 ± 0.063	0.448 ± 0.016	1.0214 ± 0.033
0.436 ± 0.033	0.445 ± 0.058	0.481 ± 0.060	2.0675 ± 0.057	0.471 ± 0.027	2.2961 ± 0.275
0.460 ± 0.014	0.813 ± 0.077	0.500 ± 0.026	4.9754 ± 0.953	0.511 ± 0.022	18.2548 ± 2.658

Fig. 2 presents plots of CO₂ partial pressure against CO₂ loading for MEA at different concentrations. To validate our data, we have compared our measurements with existing VLE data from several research groups.[5, 9] A good agreement between our VLE data and literature data shows that our setup is capable of producing reliable results. To guide the viewers, we have also fitted our measurements to a third order polynomial function (dotted lines). As can be seen from the Figure, MEA is an excellent CO₂ absorber at low CO₂ loadings and the high CO₂ solubility in MEA can be explained in regard with a rapid formation of stable carbamate complexes.

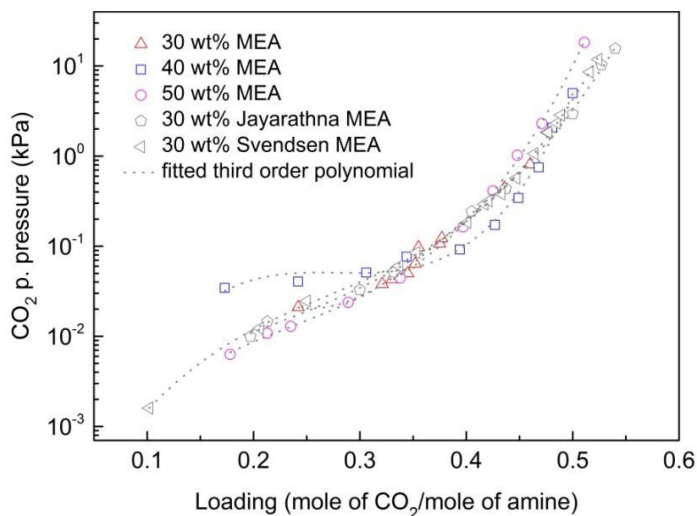


Fig. 2. VLE curves for the solubility of CO₂ in MEA solution at 40 °C. Dotted lines represent third order polynomial fitting to assist viewers.

3.2. Raman experimental results

Analysis of the species present during reactions between CO_2 and amine is desirable to better understand the process details and allow a new level of monitoring. Spectroscopic techniques offer such insight on the reaction mechanisms. Raman spectroscopy complements the existing techniques for studying liquid equilibria by providing information on intensities and band frequencies that are concentration, temperature and frequencies dependent, which would allow accurate determination of the species present during experiments. In principle, Raman spectroscopy works according to the difference in molecular polarization which determines the scattering intensity of a molecule. During our experiments, we have used deionized water for sample preparation and since the Raman scattering intensity of water is weak, utilizing Raman spectroscopy for speciation study gives the advantage we pursued.

3.2.1. Calibration plots for bicarbonate, carbonate and carbamate species

Before a thorough speciation study can be performed, it is necessary to construct trustworthy references for the species formed during the reaction of aqueous MEA and CO_2 . To begin with, we first prepared a set of different concentrations of aqueous potassium carbonate (K_2CO_3) and analyzed the spectra using our Raman spectrometer. The inset plot in Fig. 3A shows a typical spectrum recorded for aqueous K_2CO_3 . A sharp peak at approximately 1065 cm^{-1} can be detected and this peak, which is due to the symmetrical stretching of C-O bond, has been assigned by Wen and Brooker as a characteristic of CO_3^{2-} ion.[10] This particular peak can be seen to increase as the concentration of K_2CO_3 increased. Panel B shows a calibration plot for aqueous CO_3^{2-} upon analyses of the peak areas of different concentrations of CO_3^{2-} .

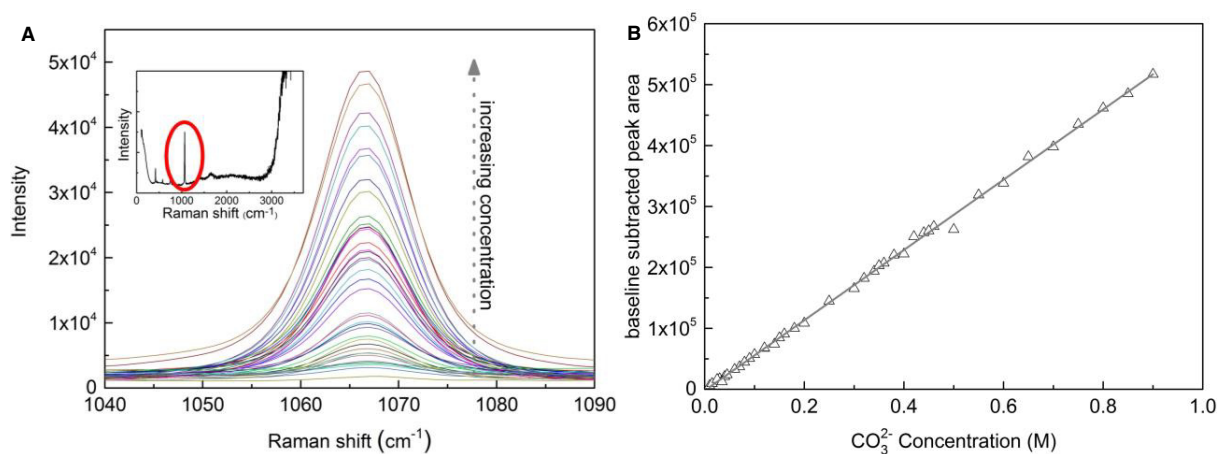


Fig. 3. (A). Spectra of carbonate ion arranged according to increasing concentration. Inset shows a typical spectrum of carbonate obtained. (B). A calibration plot of carbonate.

We then performed Raman experiments on aqueous potassium bicarbonate. A typical spectrum of bicarbonate ion is shown in Fig. 4A. The red circle with a sharp peak at approximately 1019 cm^{-1} indicates one of the characteristic bands of HCO_3^- which is due to the stretching of C-O bond.[10] As reported by Oliver and Davis, HCO_3^- is amphoteric and therefore in an aqueous solution of HCO_3^- , the presence of CO_3^{2-} can be detected and the same behavior was observed during our experiments (red asterisk symbol).[11] To take into account the decomposition of bicarbonate into carbonate in an aqueous solution, we have corrected the actual concentration of bicarbonate in the calibration plot (Panel B).

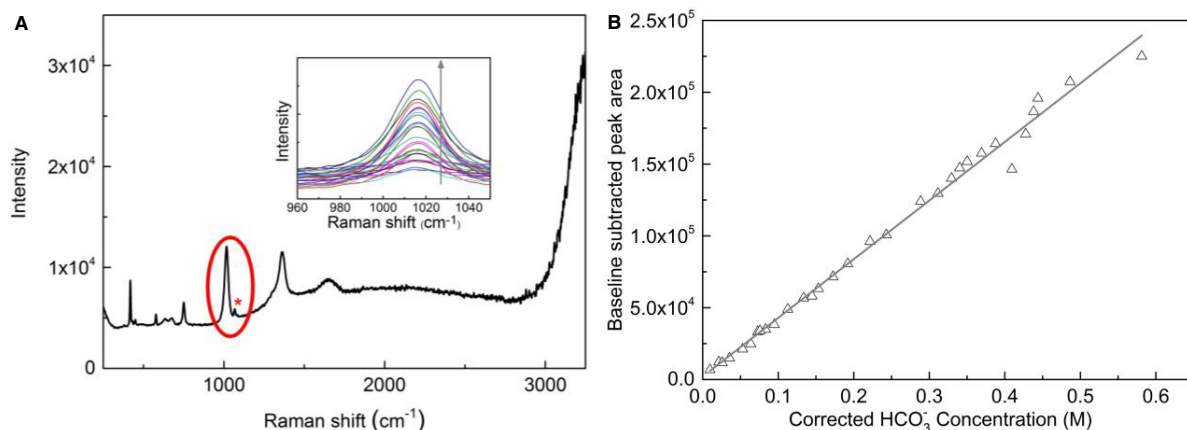


Fig. 4. (A). A typical spectrum of bicarbonate obtained. Inset shows spectra of bicarbonate ion arranged according to increasing concentration. (B). A calibration plot of bicarbonate.

Experiments to construct a calibration plot for carbamate were also conducted. A typical spectrum of aqueous carbamate is shown in Fig. 5A. A red circle on the figure indicates the most relevant region for analysis which is due to the ‘ NH_2 -wag’ of H_2NCOO^- at approximately 1034 cm^{-1} . [10] The inset figure illustrates several spectra of carbamate at different concentrations. As can be seen from the figure, carbamate in solution dissociates into carbonate and bicarbonate ions, and this information was taken into consideration upon construction of the calibration curve (Fig. 5B).

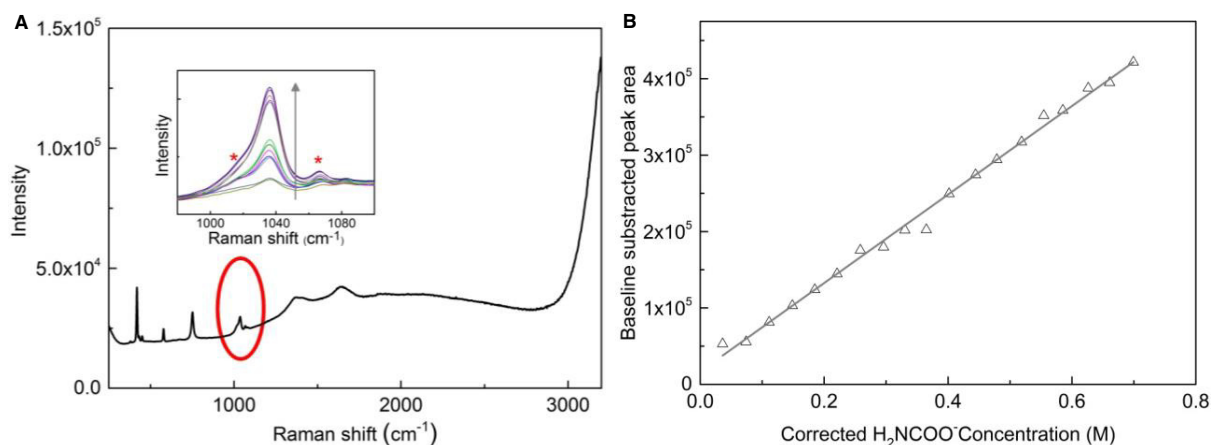


Fig. 5. (A). A typical spectrum of carbamate obtained. Inset shows spectra of carbamate ion arranged according to increasing concentration. (B). A calibration plot of carbamate.

3.2.2. Data analysis

Formation of carbonate, bicarbonate and carbamate species were monitored using Raman spectrometer and selected spectra of 30 wt% MEA samples loaded with CO_2 at different concentrations, of up to 0.436 loading, are shown in Fig. 6. As a comparison, a spectrum of aqueous 30 wt% MEA with no CO_2 is also presented. A broad bicarbonate peak at 1018 cm^{-1} may have hindered the carbamate peak at 1034 cm^{-1} from the Figure, however, as reported earlier by Souchon and coworkers, MEA-carbamate complex also has a Raman active peak at 1160 cm^{-1} and this peak is visible in our experiments. [12] Further peaks analyses using a mathematical software also revealed

the presence of a carbamate peak at approximately 1034 cm^{-1} . As can be seen from the Figure, the formation of carbonate, bicarbonate and carbamate species increased as the CO_2 -loading values increased. At 0.242 CO_2 -loading, carbamate is the main species present in the solution. Since VLE experiments were only performed using samples with CO_2 -loading values lower than 0.5 , we did not observe a decrease in the carbamate peak signal. Works are now underway in the laboratory to perform in depth quantitative analysis of the species available.

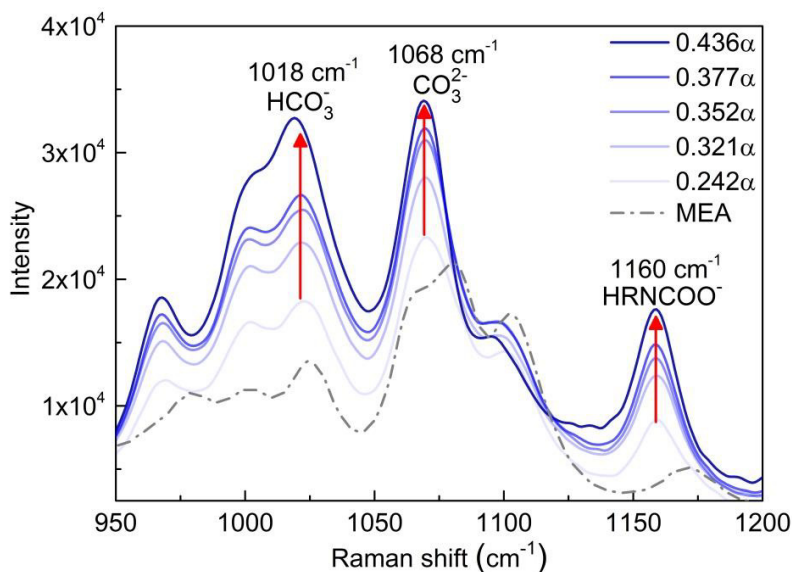


Fig. 6. Raman spectra of aqueous 30 wt% MEA loaded with different concentrations of CO_2 . Spectra are arranged according to increase in CO_2 loadings. A reference spectrum of MEA is shown as a dotted gray line.

4. Conclusion

In this paper, we have presented a new set of vapor liquid equilibrium data for MEA at 30, 40 and 50 wt% concentrations at a fixed temperature of $40\text{ }^\circ\text{C}$. These new data were compared with existing VLE data of MEA. Uncertainty evaluation performed also enables us to coherently compare our results and we have illustrated that our data correlate well with the established equilibrium data from literature. Preliminary experiments exploring the usefulness of Raman spectroscopy in quantitative analysis of the species presented in MEA- CO_2 reaction showed that this technique is robust and is able to produce reliable results.

Nomenclature

CO_2	carbon dioxide
HCl	hydrochloric acid
HCO_3^-	bicarbonate ion
CO_3^{2-}	carbonate ion
NaOH	sodium hydroxide
NH_2CO_2^-	carbamate ion
K_2CO_3	potassium carbonate
MEA	ethanolamine
MDEA	methyl diethanolamine
VLE	vapour liquid equilibrium
wt%	weight percentage

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