GHGT-12

Comparison of Liquid Phase Ion Speciation in DEAB-CO2-H2O System with IPAB-CO2-H2O System Using

^{13}C NMR Techniques

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Abstract

The ^{13}C NMR techniques were selected to investigate the ion speciation in both DEAB and IPAB solvents. Calibration equations were established to quantify the exact ion concentration of free amines and protonated amines at different absorption times. The results show that the NMR method can be used to obtain both qualitative and quantitative information of the amine-CO2-H2O system. It is also the first time to monitor the components in the new solvent (IPAB) and establish its VLE model.

1. Introduction

Carbon dioxide (CO2) capture using chemical absorption with amines has been studied for decades, but there are a number of drawbacks, such as high energy consumption for CO2 desorption and solvent regeneration, corrosion, and degradation in the presence of acid gases and oxygen.[1], which are all linked to the ion components of the amine solution. This implies that in order to improve the efficiency of CO2 capture, it is necessary to perform a comprehensive study on the speciation of both old and novel solvents. Nuclear Magnetic Resonance (NMR) technology can be used to determine both qualitatively and quantitatively analyses of all the ions in the liquid solution.[2] This makes NMR a very effective method in the development of Vapor-liquid equilibrium (VLE) model and the study of kinetics.

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Consequently, ion speciation determination using NMR techniques essentially can contribute to a better understanding of the behavior of CO_2 absorption into amine solutions.

The ion speciation in solution constitutes one of the most interesting research directions. This is because knowledge of the ions in the solution can help elucidate the circumstance behind high or low heat of regeneration of any amine solution. The NMR techniques have been applied for the detection of ions species in amine-CO_2-H_2O solutions in the field of CO_2 capture to establish or develop VLE models, as recently reviewed in detail by Shi et al.[3] and Perinu et al.[4] A convenient method proposed by Shi et al.[5] using ^{13}C NMR technology was applied for monitoring the ion speciation in 4-(diethylamine)-2-butanol (DEAB, Fig. 1a)-CO_2-H_2O system which easily separated the free amine and protonated amine. The results were compared with ion speciation obtained using the conventional method of combining pH measurements with ^{13}C NMR spectra. This new method was shown to be accurate and convenient. With this method, it is possible to directly analysis the concentrations of the main ion species of amine-CO_2-H_2O system and establish a VLE model, without the need for a pH test, thereby eliminating the need for an extra equipment and simplifying the procedure for ion speciation analysis.

4-isopropylamino-2-butanol (IPAB, Fig. 1b) is considered to be a secondary amine with a higher CO_2 absorption rate than DEAB (tertiary amine). There are two methyl groups attached to the α carbon in a IPAB molecule, which could introduce steric hindrance effects and lead to an unstable form that could reduce energy requirements for regeneration as well as corrosiveness. It has been shown that IPAB in comparison with 2-amino-2-methyl-1-propanol (AMP), methyldiethanol-amine (MDEA), monoethanolamine (MEA) and diethanolamine (DEA) has excellent performance in the CO_2 absorption process, a high CO_2 absorption and cyclic capacity as DEAB, and lower energy requirement for regeneration, compared with MEA.[6]

In this paper, the ^{13}C NMR method was utilized to monitor all ions information in the IPAB-CO_2-H_2O system. By determining all ion species, it is possible to infer the relations between molecular structure and reaction mechanism. The results can also provide useful information for further study of the kinetics behavior of the solvent system.
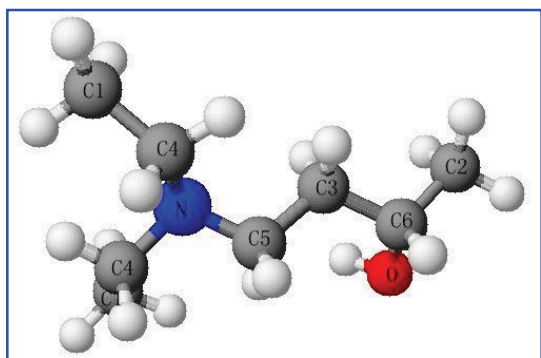

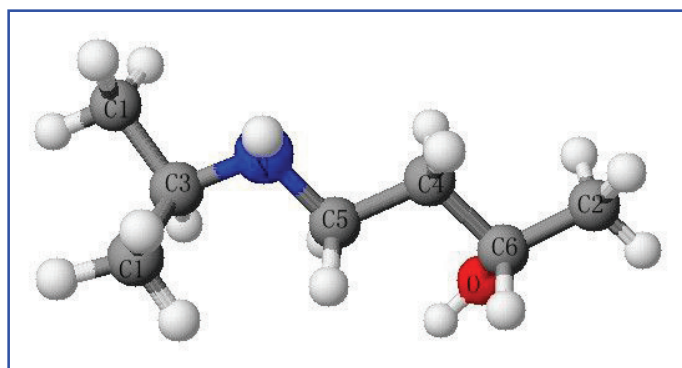Fig. 1. (a) The chemical structure of Diethylamine -2 - butanol (DEAB)

Fig. 1. (b) The chemical structure of Isopropylamine-2-butanol (IPAB)

2. Experimental

2.1 General information

CO$_2$ and N$_2$ gas (>99.9%, obtained from Fang Gang Gas Co., Changsha, China) were mixed by use of a gas mass flow meter (D08-2F, Sevenstar Electronics Co. Ltd, Beijing, China) to simulate flue gas. Isopropylamine, methanol, sodium bicarbonate, sodium carbonate deuterium oxide and 1,4-dioxane were all purchased from InnoChem Science & Technology Co. Ltd (Beijing, China). Deuterium oxide and 1,4-dioxane were used as signal lock and internal standard reference. Methyl vinyl ketone (>98%) was purchased from XiShi chemical technology company (Shanghai, China). Isopropylamine-2-butanol (IPAB) and diethylamine-2-butanol (DEAB) were both synthesized in our laboratory each with a purity of 98% measured by use of a nuclear magnetic resonance (NMR) instrument (INOVA-400, Varian company, America) and liquid chromatography-ion trap mass spectrometer (LCQ-Advantage, Thermo Finnigan, Americia). The pH measurements were carried out at 293.15 K with a pH meter (PHS-3C, Truelab Co. Ltd, Shanghai, China) calibrated with standard buffer solution at pH 4.0 (potassium hydrogen phthalate) and at pH 9.18 (sodium tetraborate). 5 mm NMR tubes produced by Wilmad Lab Glass bought from Synthware glass Co. Ltd (Beijing, China) were used for NMR tests in our experiment.

2.2 Synthesis of new solvents（4-isopropylamino-2-butanol）

The synthesis process was performed following the procedure in the patent proposed by Tontiwachwuthikul et al.[6] At the beginning, 65 mL vinyl ketone was put in a constant pressure dropping funnel which allowed it to be added slowly in a drop wise manner into 70 mL of neat diethylamine or isopropylamine that was placed into an ice bath. The ice bath was removed after the final drop which was in about 1h. Then, the solution was stirred at room environment for another 3 h; 30 mL of methanol and 26 g borohydride was added slowly at ice bath temperature for 1h. After that, stirring continued at room temperature for 3 h. Finally 30 mL water was added and the mixture was stirred for an extra 1 h, and then stirring was continued at room temperature for 3 h. Then 30 mL of water was added and the mixture was stirred for an additional 1 h; the mixture was then filtered with a buchuel funnel, and washed with (dichloromethane) before distillation to purify the product. The product was determined by NMR instrument.

2.3 Calibration of Mass flow meter

To ensure an accurate mixed ratio of between CO$_2$ and N$_2$, a lather flow meter with a volume of 100 mL was used to correct the displayed value. Experimental setup is shown in Figure 5. The gas valve was open and the flow rate of CO$_2$ was adjusted to within the range of 50 ml / min (maximum flow rate). Then a bubble was squeezed out through the plastic head at the bottom of lather flow meter. Then the displayed value was put on the mass flow meter and the actual measured value into a x,y coordinate system in which x represents the horizontal axis (displayed valued), y represents vertical axis (real value). The result is shown in Figure 6 and 7. The desired mixed ratio of gas can be obtained by the calibration equation of CO$_2$ and N$_2$.

The calibration process was performed at atmospheric conditions and the following two calibration equations were obtained:

$$y_{CO_2} = 1.5273 x_{CO_2} - 0.1800$$

$$y_{N_2} = 1.1134 x_{N_2} - 0.1961$$

x is the real value and y is the displayed value on the gas mass flow meter.

According to calibration equations we can obtain an r accurate ratio of mixed gas. In our work we set up the flow rate CO$_2$ 40.0 (displayed rate) N$_2$ 227 (displayed value).

2.4 The Validation of Deviations of NMR Calibration

In this work, we also did the comparison of NMR instrument with that used by Shi et al.[5] in which the only difference of above experimental conditions was the difference in temperature (293.15 K, our work; 297.65 K by Shi et al.[5]). Also, and we generated additional 5 points to cover all the range of ratio of DEABH[+]/DEAB (0-1). Table 1 shows the chemical shifts changes with the ratio of DEABH[+] / DEAB, and according to the carbon signals that moved to upfield, was proved to show a linear relationship between chemical shifts and the ratio of protonation of the amine. The calibration equation is shown in Fig. 2 and 3.

2.5 CO₂ absorption process

A four-neck round bottom flask was used for CO_2 absorption. It was equipped with a bubbling tube, a thermometer, a pH electrode, as well as a trachea. The absorption experiment was carried out at 293.15 K and standard atmospheric pressure with amine concentration at 1.5 M (IPAB). The desired absorption temperature was controlled by a thermostated water bath. CO_2 and N_2 were mixed and bubbled into deionized water before being injected into the amine solution at a flow rate of 26.3 mL/min and 204 mL/min (mixed ration about 12%). A pH meter was also simultaneously used to monitor the pH changes. The outlet gas was released from the top of the absorber. In order to obtain an accurate and stable pH value, a 5 cm magnetic stirrer was used with a stirring speed of 1000 r/min.

2.6 The concentration of ion species in amine-CO₂-H₂O system

$$\frac{[NH_2CO_2^-]}{[HCO_3^-]+[CO_3^{2-}]} = R$$

$$[NH_2CO_2^-] = \frac{R}{1+R} \times [CO_2]_0$$

$$[CO_3^{2-}] = \frac{\delta - 160.33}{(169.09 - 160.33) \times (1+R)} \times [CO_2]_0$$

$$[HCO_3^-] = \frac{169.09 - \delta}{(169.09 - 160.33) \times (1+R)} \times [CO_2]_0$$

The above equation was proposed by Homles et al.[7] combining chemical shifts and peak area integration to calculate the concentration of carbonate, bicarbonate, carbamate in ammonia/CO_2/H_2O system. But it did not give the concentration of protonated ammonia and free ammonia. Shi et al.[5] proposed a method in which chemical shifs were applied into calculating the concentration of amine and protonated amine. So in our work, both methodologies were used to quantify amine, protonated amine, carbamate, carbonate, and bicarbonate.

The NMR spectrum of amine/CO_2/H_2O system was obtained with a Varian 400 MHz NMR instrument. About 10% deuterium oxide was used as signal lock and drops of 1,4-dioxane was used as an internal standard. To obtain a valid result of the carbamate peak to the area under the carbonate/bicarbonate peak, there must set up a suitable relaxation time to ensure the effect of NOE had been absent. This is a reasonable expectation because there are no hydrogen atom bonded directly to the carbon atom.[6] In our work the Reverse gated decoupling techniques was selected to reduce NOE effect and quantify the ion species in solution. Delay times between pulses of five to six times the spin-lattice

relaxation times was recommended for use for the measurement of the ^{13}C NMR spectrum.[6] But five to six times the spin-lattice relaxation times would have led to a very long acquisition time with a certain number of scans. Homles compared the result obtained by a 5s delay time with a 180s only 6% variation was obtained. So, all ^{13}C NMR spectra in our work, was collected with a delay time of 5s.

3. Results and discussion

3.1 Validation of Deviations of NMR Calibration

A series of samples of aqueous DEAB and IPAB solvents at 293.15 K were titrated by different amounts of HCl and was selcted and analyzed on the NMR instrument to establish the calibration curves of C_1, C_3, C_6 plotted in Fig. 3.
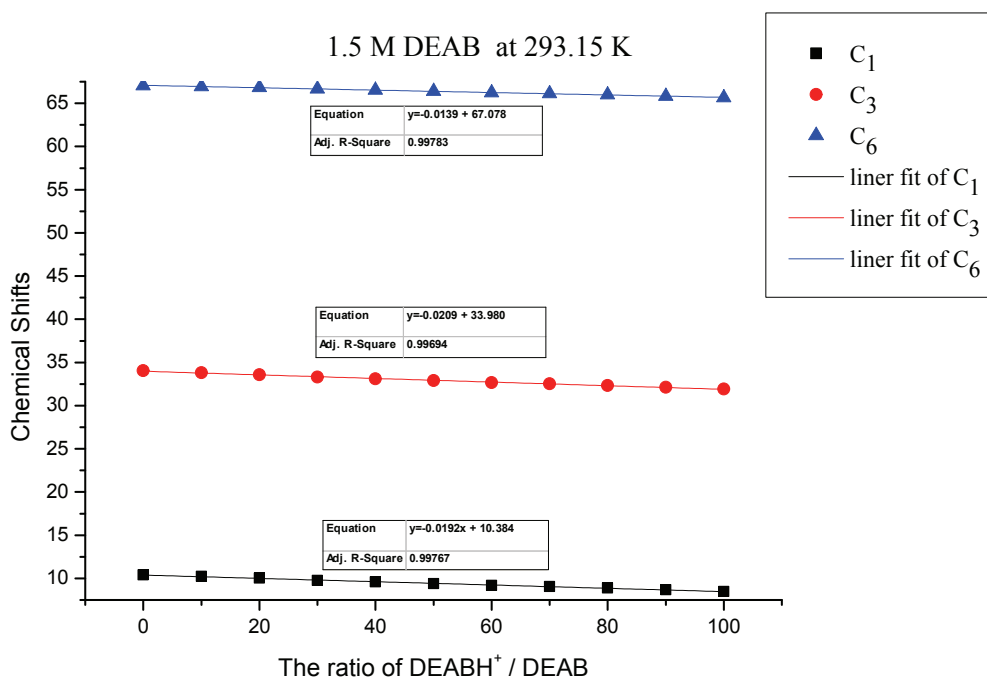

Fig 2. a series of NMR calibration curves of DEAB at 293.15 K with a concentration of 1.5 M.

Tables 1 and 2 list the validity and deviation of the calibration methods for aqueous DEAB and IPAB solutions respectively. The protonation rate by titration as a reference standard is listed in the left column. The results of the protonation ratio (x) obtained by the acquired chemical shifts of DEABH$^+$/DEAB and IPABH$^+$/IPAB are in Tables 1 and 2. The calibration results are also listed in the right column including the absolute deviations marked by "D%" of the calibration method. On the other side, in order to generate a more accurate calibration result, three carbons which will move to upfield obviously were selected to make a comparison and finally choose the most accurate one that is used in amine-CO_2-H_2O system to calculate the equilibrium concentration of the free amine and protonated amine.

Table 1. Validation of Deviations of NMR Calibration for DEAB

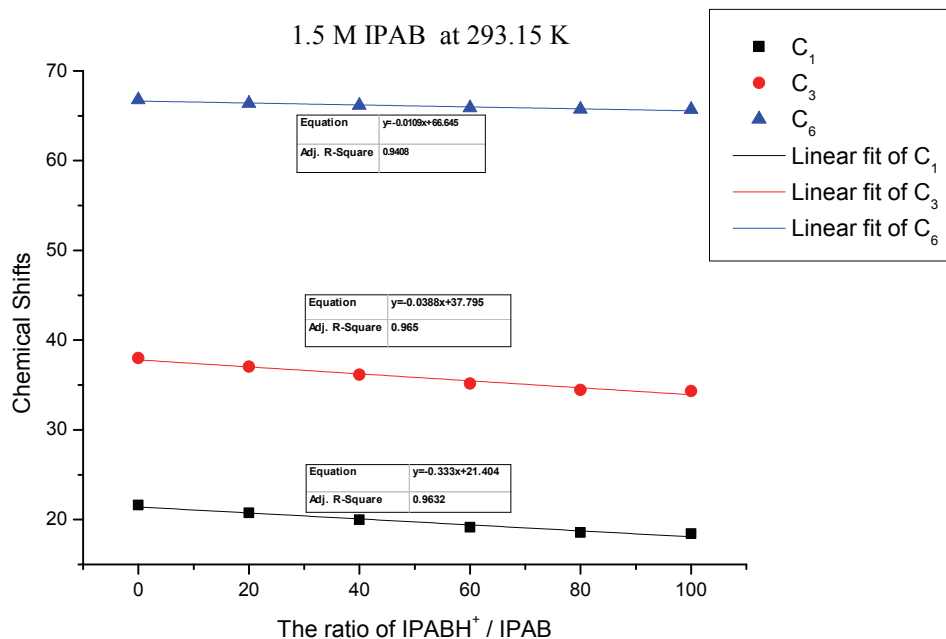| titration ratio of DEAB (%)	Protonation of DEAB					
	by NMR Calibration(C_1)	D%	by NMR Calibration(C_3)	D%	by NMR Calibration(C_6)	D%
0	-1.72	-1.72	-2.58	2.58	2.66	2.66
10	8.59	-14.10	8.71	-1.29	10.29	2.90
20	19.32	-3.40	19.67	-1.65	17.99	-1.01
30	32.03	6.77	32.44	8.13	30.07	0.23
40	41.2	3.00	41.91	4.78	39.42	-1.45
50	51.51	3.02	51.77	3.54	49.28	-1.44
60	62.24	3.73	62.39	3.98	60.79	1.32
70	69.01	-1.41	68.95	-1.50	67.91	-2.99
80	78.91	-1.36	79.52	-0.60	80.00	0
90	88.85	-1.28	89.04	-1.07	91.00	1.11
100	98.8	1.20	98.85	-1.15	101.94	1.94
average		3.72		2.75		1.55

Fig 3. a series of NMR calibration curves of IPAB at 293.15 K with a concentration of 1.5 M.

Table 2. Validation of Deviations of NMR Calibration for IPAB

titration ratio of IPAB (%)	Protonation of IPAB					
	by NMR Calibration(C_1)	D%	by NMR Calibration(C_3)	D%	by NMR Calibration(C_6)	D%
0	-6.07	-6.07	-5.51	-5.51	-11.65	-11.65
20	19.70	-1.50	19.28	-3.61	25.14	25.69
40	42.94	7.36	42.71	6.76	44.86	12.16
60	68.26	13.76	68.27	13.79	68.44	14.07
80	85.74	7.17	85.95	7.44	84.77	5.96
100	89.04	-10.96	89.41	-10.59	87.43	-12.57

3.2 The analysis of IPAB-CO₂-H₂O system

After the effectiveness of NMR method was validated (proved in the section 2), it was utilized to monitor the ion species in IPAB-CO_2-H_2O system. Several ^{13}C NMR spectra at different CO_2 loading were collected at 20℃ on a 400 MHz Varian NMR spectrometers and the changes of ion species in the amine (IPAB) solution were recorded. The concentration of the main ion species can be seen in Fig. 4. It can be seen from the spectrum that the signals of IPAB-CO_2-H_2O system and DEAB-CO_2-H_2O system were complex due to relatively complex structure of IPAB and DEAB molecules in which there are more carbon atoms including asymmetric carbon atoms in both IPAB and DEAB. So the peak intensity of those asymmertic carbon atoms should overlap in theory.

No carbamate or carbonate/bicarbonate singles were detected at the beginning of absorption within the range of CO_2 loading of 0-0.15, which can be explained by the fact that the amounts of the ions are too small to be detected by the NMR instrument. On the other hand, there is only one peak in the range of 160-170 ppm, which represents HCO_3^-/CO_3^{2-}. Another six peaks in the range of 0-70 ppm represent $IPABH^+$/IPAB that was not separated, which can be explained by the fast changing rate of proton (H^+) in the solution. The formation of carbamate due to the reaction of IPAB with CO_2 was not detected in the IPAB-CO_2-H_2O system. This can be explained by the chemical structure in which there are two methyl detected to the α carbon atom. but IPAB has a faster CO_2 absorption rate than DEAB. The unstable carbomate can reduce the energy requirements.

The comparison between DEAB-CO_2-H_2O System and IPAB-CO_2-H_2O System thus helps us to better understand the reaction mechanisms which will help to appropriately select a solvent that can improve the CO_2 absorption rate and reducing energy consumption.

4. Conclusions

The validation test of NMR calibration test were performed based on 1.5 M aqueous DEAB solvents. The results showed that the NMR calibration test showed a high accuracy of about 99.7%. Compared with the titration ratio as a reference standard, the quantitative results of free amine and protonated amine exhibitted a deviation of about 3% in protonated DEAB solution and about 10% in protonated IPAB solution. Then the NMR calibration method can be applied into the IPAB-CO_2-H_2O system for a VLE model analysis at room temperature to generate a useful database. For NMR calibration, it is very important to perform NMR peaks calibration first, and then perform peak assignment, peak area

integration, zero line correction onto spectra interpretation, and data calculation to generate good ion speciation data.
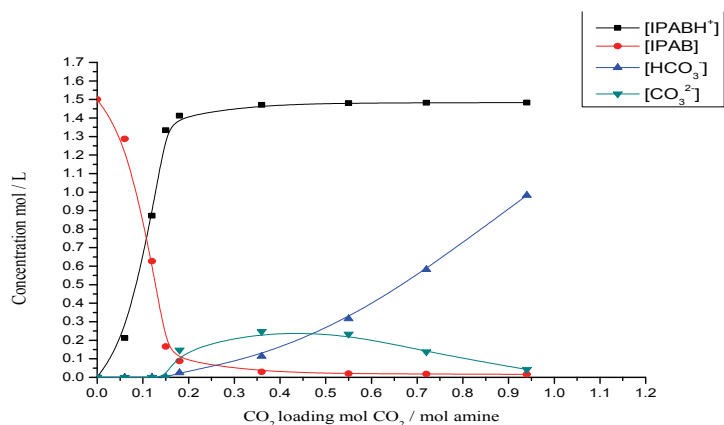

Fig 4. Ions concentration in IPAB-CO_2-H_2O system

Acknowledgements

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