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Relationship Between pH and Carbonation Ratio to Measure CO_2 Capture Efficiency by NH_3 Solvent

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This paper presents an established relationship between the pH of ammonia solution and its carbonation ratio (α). The aim of this correlation is to track the amount of CO_2 absorbed or the amount of CO_2 released from ammonia solvent. Furthermore, this paper studies the evolution of density and viscosity of ammonia solution with the carbonation ratio because those physical properties can significantly affect liquid side mass transfer coefficient. Experiments have been carried out in a thermoregulated Lewis-type cell reactor and the measures have been done using three concentrations of ammonia (3, 5 and 7 wt %) and temperatures (293, 303 and 313 K). Results show that the estimated function has a high correlation coefficient which indicates a relationship between variables. All results show a linear correlation between viscosity and carbonation ratio, and between density and carbonation ratio.

1. Introduction

Carbon dioxide has been spotted as a main contributor in greenhouse effects. Recent research is focused on reducing CO_2 released in the atmosphere, both from existing power plants and from the ones that will be built to meet world's population increasing need of energy (Agency, 2009). CO_2 capture of power plants represents from 40 to 60 % of global cost in the process of CO_2 capture and storage (CCS). Chemical absorption from post combustion gases is the main method that would be considered in CCS. CO_2 capture steps are split in two parts, first CO_2 absorption by a solvent, frequently amines, and second regeneration of solvent and release of CO_2 by heating. This last part requires a lot of energy and it depends on the solvent used to capture CO_2. Among the employed amines, Monoethanolamine (MEA) is the most widely used due to its high reactivity with CO_2 compared to the other alkanolamines (Rodriguez, 2011). Nevertheless, this solvent is corrosive and it has high energy requirements on regeneration process. In addition, researches have been devoted to find or to develop better solvents in terms of reactivity and energy consummation.

Ammonia seems to be an alternative solvent for removing CO_2 from flue gases (Gonzales-Garza et al., 2009). Indeed, it presents a higher loading capacity than MEA and it has low cost production. Furthermore, the use of NH_3 may reduce regeneration costs (Molina and Bouallou, 2010). In order to evaluate process efficiency of CO_2 absorption by ammonia, gas compositions at the inlet and outlet of the absorber and stripper are frequently measured. However, this measurement does not indicate liquid phase behavior. Indeed when CO_2 is absorbed "carbonation ratio" increases, which is the solvent fraction reacting with CO_2 (Eq. 1).

$$\alpha = \frac{Quantity\ of\ CO_2\ (mol)}{Quantity\ of\ NH_3\ (mol)} \tag{1}$$

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The pH's measurement related to CO_2 liquid composition at the inlet and outlet of the absorber and stripper. The data relating the pH to carbonation ratio can be found in several studies in the literature only for MEA solvent (Vanichseni, 1977, Koonaphapdeelert et al., 2009; Chabanon et al., 2011).

The aim of this study is to establish a relationship between pH of ammonia solution and carbonation ratio (α) which tracks the amount of CO_2 absorbed or the amount of CO_2 released. Furthermore, this paper studies physical properties (density and viscosity) evolution of ammonia solution with the carbonation ratio because these physical properties can be significantly affect liquid side mass transfer coefficient. Since the pH measurements of the solution depend on temperature (even with temperature compensated pH meters), pH electrodes were tested at different temperatures as well as at different NH_3 concentrations.

2. Materials and methods

2.1 Description of the materials

Experiments were carried out in a closed reactor of the Lewis cell type (Figure 1). Lewis cell can be used for acid gases absorption or desorption experiments (Cadours et al., 1997).This system enables to follow the evolution of pressure easily, while maintaining temperature constant and creating an optimum contact between the gaseous and the liquid phases.

This device consists of a Pyrex glass jacket allowing circulation of a temperature controller fluid. The upper bracket includes a pressure sensor that monitors the change in pressure over time in the gaseous phase. The lower flange includes a probe that measures the temperature of the liquid phase at any moment, and a valve enabling to load the solution. The agitation of the gas phase is accomplished by a propeller driven by a magnet bar located inside the cell and set in motion by a magnetic stirrer located outside the cell. The magnetic stirring of the liquid phase is provided by a Rushton turbine. The cell's volume is of about 369.5 mL. The interfacial surface area was 15.34 cm^2.

At the bottom of the cell, the solution is taking by a sampling device. Through a micro tube of polytetrafluoroethylene fitted with a 2-way valve which contains an O-ring for sealing, samples of the liquid phase can be taken in a syringe, in order to study the evolution of the solution's properties.

The data of interest is collected and analyzed using dedicated software (Benchlink Data Logger). The main acquired readings are pressure and temperature, both in the Lewis cell and in the carbon dioxide reservoir. Once the absorption process is initiated, the data is collected and evaluated on real-time.

2.2 Description of the experiments

Temperature (T) and ammonia concentration (C_{NH3}) are set based on previous experiments conducted in the laboratory, and on simulations that have been performed using the Aspen software. They allow us to perform sensitivity studies, particularly for CO_2 capture to fired power plant application (Molina and Bouallou, 2010). From there, we can determine temperature and concentration ranges needed to be studied in priority. Nine series of experiments were conducted, under the following conditions.

Table 1: Ammonia concentration and temperature conditions for the different experiments

Experimental conditions	(C_{NH3},T)	Experimental Conditions	(C_{NH3},T)	Experimental conditions	(C_{NH3},T)
A1	5 wt%; 293 K	B1	3 wt%; 293 K	C1	7 wt%; 293 K
A2	5 wt%; 303 K	B2	3 wt%; 303 K	C2	7 wt%; 303 K
A3	5 wt%; 313 K	B3	3 wt%; 313 K	C3	7 wt%; 313 K

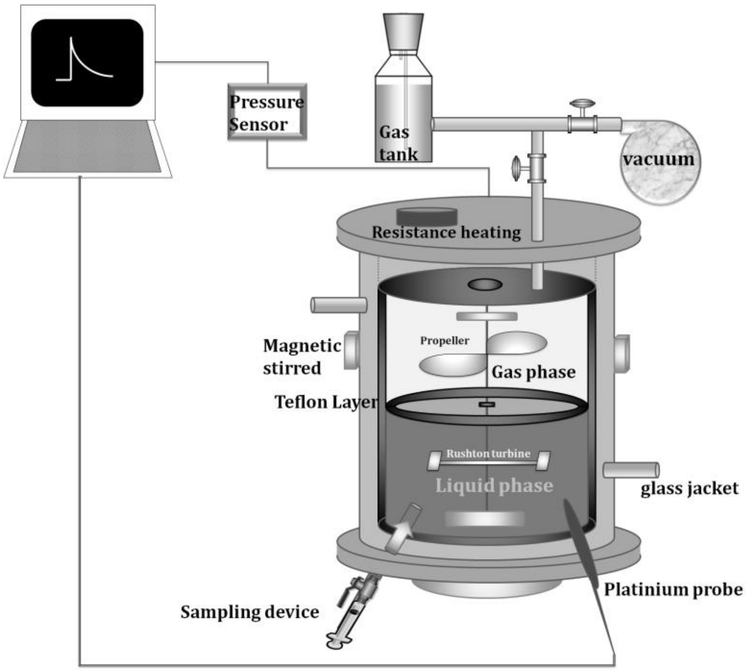

Figure 1: Scheme of experimental device

A diluted solution of ammonia (3, 5 or 7 wt %) was first prepared from a concentrated solution (20 wt %) in a vacuumed round-bottom flask. This flask is weighted between each step on a precision balance. The molar quantity of NH_3 in the reactor can be inferred from the mass of solution injected in the Lewis cell.

For each step of the experiment, the molar quantity of CO_2 to be injected into the cell is linked to the required carbonation ratio α. The related variation of pressure in the carbon dioxide's tank is computed from the ideal gas law.

The required amount of CO_2 is added into the reactor, where it is absorbed by the ammonia solution.

When equilibrium is reached, a sample of the ammonia solution is taken (1 mL) in order to measure its pH. A new injection of CO_2 is done using the same method, and so on. The sample of solution can also be used to examine the variations in viscosity and density of the solution.

The actual loading rate is calculated using pressure changes in the Lewis cell data, assimilating carbon dioxide to a perfect gas. For each injection, a (α, pH) couple at a given temperature is obtained. A curve representing α as a function of pH is drawn from the series of points.

2.3 Repeatability and reproducibility of pH measurements and experiences

The accuracy of our pH measurements was assessed through the study of the repeatability and reproducibility of our manipulations. The inherent precision of the measurement equipment was evaluated through 8 successive pH measurements of the same sample, in the exact same conditions of temperature, with the same operator using the same pH-meter (Table 2).

The standard deviation obtained was 0.02, which means that pH-meter is reliable. Concerning the reproducibility evaluation, we chose to study the influence of measurement instrument. Two different pH-meters have been used to measure nine solutions samples. The average of standard deviation was around 0.05.

Table 2: Multiple measurements of a single sample under similar conditions

Measurement	pH
1	8.98
2	8.99
3	8.99
4	9.02
5	9.03
6	9.02
7	9.02
8	9.03
Standard deviation	0.02

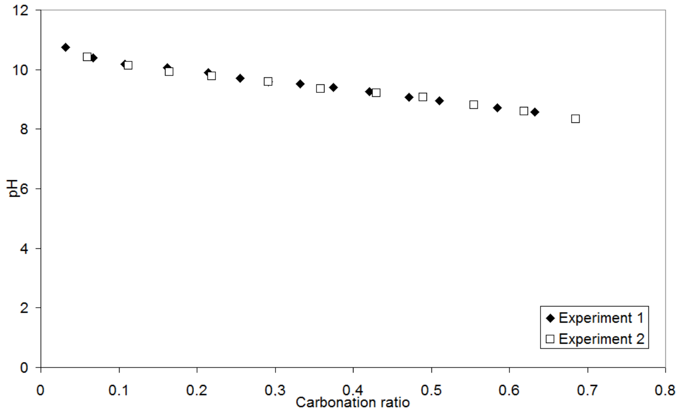

Figure 2: Results of experiments studying influence of carbonation ratio on pH, NH_3 = 3wt%, T= 303K

Figure 2 shows reproducibility of experience. Both experiences show the same trend and there is no Offset between them. Thus we can validate that the experience is reproducible. Experiments 1 and 2 were conducted at 303 K, with concentration of 3 %wt, in ammonia.

3. Results and Discussion

Figure 3 and Figure 4 show the influence of concentration and temperature on pH and carbonation ratio. The general trend is the same as the one observed by Disli (1996).

Figure 3 illustrates three experiments conducted at 313 K, with concentration of 3 wt%, 5 wt% and 7 wt% in ammonia. Similar tests have been run for 293 K and 303 K (data not shown). It appears that pH is a negative function of NH_3 concentration, which is consistent with the MEA results. Which means at any given carbonation ratio, the higher the concentration in ammonia is, the lower the pH is.
In Figure 4, the concentration is set at 7 wt% and the influence of temperature is studied. Concentrations of 3 wt% and 5 wt% gave similar results (data not shown). The experiment shows that pH is a negative function of temperature. Both observations are therefore coherent with the MEA correlation. It can be inferred from these results that both, ammonia concentration and temperature, have an influence on the pH of the solution, and that both should therefore be taken into account when trying to find a correlation between pH and carbonation ratio. Data also show that pH is a negative function of both NH_3 concentration and temperature, meaning that a negative sign will appear in front of both terms in the correlation.

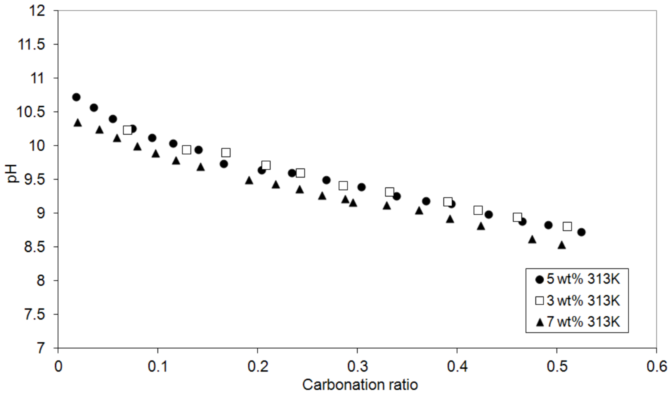

Figure 3: Results of experiments studying influence of concentration on pH and carbonation ratio

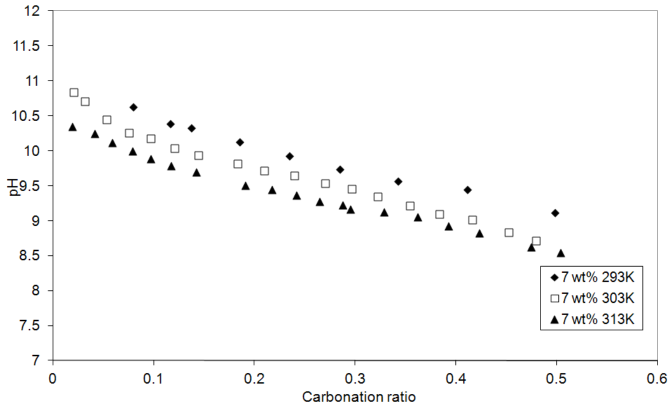

Figure 4: Results of experiments studying influence temperature on pH and carbonation ratio

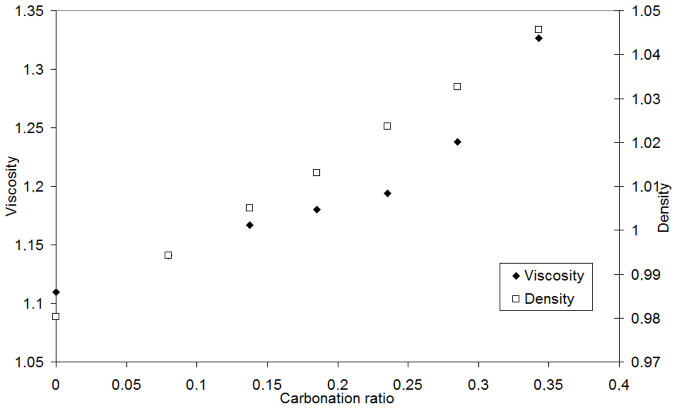

Figure 5: Results of experiments studying influence of carbonation ratio on density and viscosity NH_3 = 7 wt%, T= 293 K

Evolution of the physical properties of the ammonia solution with the carbonation ratio is monitored and shown above. Figure 5 shows kinematic viscosity and density as functions of the carbonation ratio. Both are found to linearly increase with α. Measures were done on all three concentrations and all three temperatures (data not shown). All results show a linear correlation between viscosity and α, and between density and α.

All results were gathered in order to establish a correlation between carbonation ratio, temperature, pH and ammonia concentration. Similarly to Vanichseni, (1977) and Disli (1996), a linear correlation was postulated. The aim was then to numerically determine coefficients m_1, m_2 and m_3 of the following formula (Eq. 2):

$$\alpha = m_1 * pH + m_2 * T(k) + m_3 C_{NH_3}(wt) + b \tag{2}$$

Table 3: Coefficients data

	m_3	m_2	m_1	b
m coefficients	-0.9638	-0.0057	-0.2689	4.6397
Standard deviation	0.2270	0.0005	0.0062	0.16562

The correlation coefficient is 0.9326, while the average error of estimate the carbonation ratio (α) is 0.0407.

4. Conclusions

The behavior of the solvent during absorption desorption is an important factor to determine if ammonia solution is saturated (high carbonation ratio) or if it is well regenerated. Indeed, the energy used to regenerate ammonia is an essential parameter to design a CO_2 capture unit. For this reason, we have established a correlation between carbonation ratio and pH of ammonia solution to measure the effectiveness of absorption and regeneration. The estimated function has a high correlation coefficient which indicates a relationship between variables.

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