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Correlating the physical solubility of CO_2 in several amines to the concentrations of amine groups

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ABSTRACT

In this study, the physical solubilities of CO_2 in several amine solutions at different concentrations and pressures were determined using the nitrous oxide N_2O analogy. The solubilities of N_2O in four aqueous amine solutions, including Monoethanolamine (MEA), Diethanolamine (DEA), Diethylenetriamine (DETA), and Tetraethylenepentamine (TEPA) were determined experimentally at different concentrations and pressures ranging from 1 to 4 kmol/m^3 and 101.3–405.3 kPa, respectively. The solubility of N_2O and CO_2 for a few amines were compared with data available in the literature. The experimental data agreed well with those published in the literature. The CO_2 solubility values obtained experimentally as well as other values from the literature were correlated to the concentrations of the amino groups in the amine. The physical solubility of CO_2 was found to be inversely proportional to the number of amino groups in the amine. The simple correlation can give reasonable predictions with an average error of less than 10% for CO_2 solubility at 298 K and 101.3 kPa.

1. Introduction

During this past decade, extensive amount of research have been devoted to the evaluation of the solubility of acid gases in amines solutions considering the amines' loading capacities and reactivity. Consequently, considerable amount of data for the solubility of these gases in common amines have been published in the literature, including solubility data in primary, secondary and tertiary amines focusing on the amine blends to maximize the desirable qualities of the individual amines (Penttilä et al., 2011). Although solubility data may be available in the literature for well-known amines, it is rather scarce or not accessible for less known amines that may prove to be effective solvents for the removal of these acid gases. Diethylenetriamine (DETA) (Hartono et al., 2009; Al-Marzouqi et al., 2009), and tetraethylenepentamine (TEPA) (Al-Marzouqi et al., 2009; Aronu et al., 2009, 2011; Wang et al., 2013) are among some novel amines which have been recently considered as promising alternative solvents for CO_2 capture. To the best of the authors' knowledge, there are no reports in the open literature on the effect of pressure on the physical solubility of CO_2 in DETA or TEPA. In fact, the authors were unable to find any reported data for the CO_2 solubility in TEPA even at ambient conditions. Moreover, most solubility data in the literature were evaluated at atmospheric pressures in spite of the need for high pressure data to be used in real engineering applications such as the design of amine absorption towers for the sweetening of natural gas. A recent study has evaluated the potential of acid gases removal at elevated pressures of up to 50 bar using hollow fiber membrane contactors (Marzouk et al., 2010). Experimental evaluation of physical properties such as solubility data at different operating conditions and the development of reliable correlations for these data are essential in the formulation of comprehensive models for predicting and simulating acid gas removal from natural gas or biogas (El-Naas et al., 2010; Faiz et al., 2011; Zhang et al., 2014a, 2014b).

The main objective of the present study was to experimentally evaluate the physical solubility of CO_2 in several important amines (MEA, DEA, DETA and TEPA) at different concentrations and different pressures and to correlate the collected experimental data and those reported in the literature to the concentrations of the amine groups.

2. Experimental methods

Solubility data were obtained for CO_2 and N_2O in distilled water

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and for N_2O in Monoethanolamine (MEA), Diethanolamine (DEA), Diethylentriamine (DETA) and Tetraethylenepentamine (TEPA) at different amine concentrations ranging from 1 to 4 kmol/m^3 at 298 K and different pressures ranging from 101.325 to 405.3 kPa. The experimental results presented in the next sections are based on averaging duplicated experimental runs for all conditions, with the standard deviation ranging from 2 to 5% of the reported average.

2.1. Apparatus and procedure

The solubility experiments were conducted using a specially built glass reactor/solubility cell (Model R-211), purchased from Labkorea, Soul, South Korea. The cell has a total volume of 1.902 L and a set maximum pressure of 75 psi. The system was connected to a desktop computer through a data acquisition card to provide direct measurements of both temperature and pressure inside the cell. A water bath was used for temperature control through continuous circulation of water at the desired set temperature. A schematic diagram of the solubility cell is shown in Fig. 1. An exact volume of 0.10 L of the desired solution was fed to the cell by air evacuation using a vacuum pump. The solution was then degassed under vacuum. Once the degassing process was completed, the desired gas (CO_2 or N_2O) was fed to the cell until the required initial pressure was reached. Stirring was then started using the built-in magnetic stirrer until the equilibrium pressure stabilized. The initial and equilibrium pressures were recorded for each experimental run.

2.2. Solubility calculations

The N_2O solubility was calculated according to the following equations:

$$N_{gas} = \frac{(P_i - P_{eq}) \cdot Vg}{R \cdot T} \quad (1)$$

$$H = \frac{P_{eq}}{C} \quad (2)$$

where P_i, P_{eq} are the absolute initial and equilibrium pressures in kPa. H is Henry's constant in kPa.m^3/kmol and C is the concentration of the dissolved gas in liquid, in kmol/m^3. N_{gas} represents the number of moles of gas dissolved in the liquid, in kmol, and Vg represent the volume of the gas in the cell.

Since CO_2 reacts with aqueous alkanolamine solutions, its solubility cannot be measured directly (Penttilä et al., 2011), and N_2O analogy experiments can be carried out as originally proposed by Clarke (Clarke, 1964). In view of the similarities between the CO_2 and N_2O with regard to configuration, molecular volume, and electronic structure, the ratio of the solubility of nitrous oxide in a given solvent to that of carbon dioxide in the same solvent is considered to be constant at a given temperature. The solubility of CO_2 in aqueous amine solutions is then estimated from the ratio of the solubility of CO_2 and N_2O in water in combination with the data for the solubility of N_2O in these particular solutions. This analogy can be formulated as follows:

$$H_{CO_2,Amine} = H_{N_2O,Amine} \cdot \left(\frac{H_{CO_2,H_2O}}{H_{N_2O,H_2O}} \right) \quad (3)$$

3. Results and discussion

To validate the apparatus, the solubility of CO_2 and N_2O in water at 298 K and at 101.325–405.3 kPa were measured. The results are compared with those reported in the literature and presented in Table 1. It can be clearly noticed that the experimental data are in a good agreement with the data from the literature, which confirms the accuracy and reliability of the experimental unit. The evaluated ratio of the solubility of CO_2 to that of N_2O in water was about 0.759; whereas the average value in the literature was 0.740 (Jou et al., 1992).

The solubility of N_2O in MEA, DEA, DETA and TEPA were obtained over the ranges: 1–4 kmol/m^3 and 101.325–405.3 kPa. All measurements were made at a temperature of 298 K. The estimated

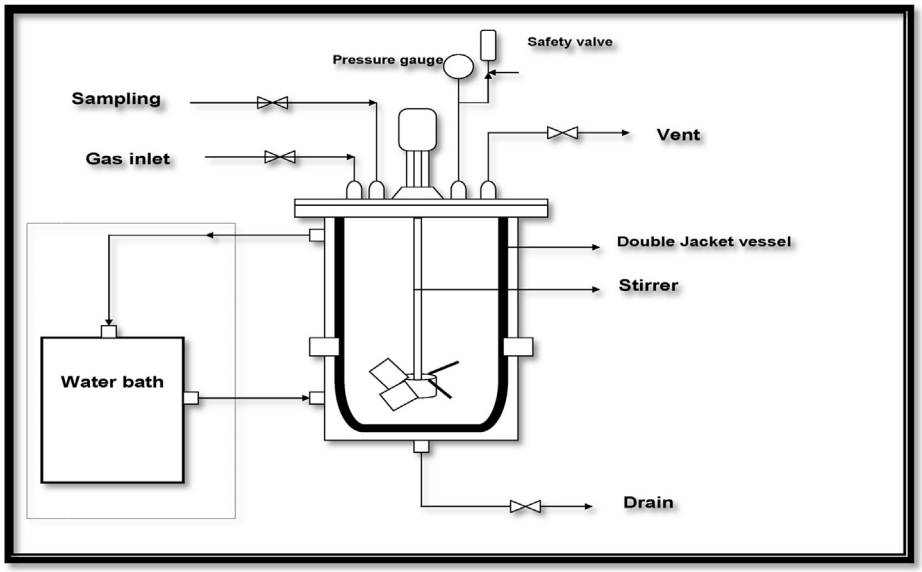

Fig. 1. A schematic diagram of the stirred glass reactor.