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Experimental measurements and modelling of carbon dioxide solubility in aqueous AMP/MDEA and Piperazine/MDEA blends

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ABSTRACT

Experimental measurements and modelling of carbon dioxide solubility were performed in separate aqueous blends of 2-amino-2-methyl-1-propanol (AMP)/N-methyldiethanolamine (MDEA) and piperazine (PZ)/MDEA in the high gas loading region. The experimental loadings of carbon dioxide were measured at various parametric values of pressure (102.5–4110 kPa), temperature (303.15–343.15 K) and solvent concentration (1 + 1 and 2 + 2 M). It is shown that addition of AMP and PZ to MDEA improved the overall carbon dioxide loadings and were in excellent agreement with the experimental values found in open literature. The experimental results were accurately correlated by a hybrid Kent–Eisenberg model, with an average deviation of 10.5%. Furthermore, the model satisfactorily estimated the carbon dioxide solubilities in AMP/MDEA and PZ/MDEA blends at other parametric conditions.

1. Introduction

Separation of carbon dioxide from natural gas streams has become an imperative step in oil and gas sector. Chemical absorption via alkanolamines has been widely used for this purpose. The use of N-methyldiethanolamine (MDEA) has passively increased due to its better performance, compared to classical alkanolamines like monoethanolamine (MEA) and diethanolamine (DEA) [1]. However, low absorption rate of MDEA desires a larger absorption column and adversely affects capital and operational costs [2]. Therefore, blends of MDEA with different alkanolamines have been tested under laboratory conditions for optimal absorption rate, absorption capacity and heat of solvent regeneration. This for example, includes separate blends of MDEA with MEA and DEA which were widely investigated in literature [3–8]. On the other hand, blends of 2-amino-2-methyl-1-propanol (AMP) and MDEA, and piperazine (PZ) with MDEA were inadequately studied. Xu et al. [9], Liu et al. [10] and Bishnoi and Rochelle [11] generated experimental data for low gas loading region of PZ/MDEA solutions. The results were compared and a model was developed by Kamps et al. [12]. The work was extended by Ali and Aroua [13] for studying the effect of small amount of piperazine on MDEA solutions at low pressure. Derks et al. [14] studied the effect of piperazine on MDEA solutions for carbon dioxide solubility for pressures near to atmospheric conditions. Hosseini Jenab et al. [15] and Matin et al. [16] studied the PZ/MDEA systems for high loading-high pressure region (0.03–4 MPa) using a Debye-Huckel based model. Jang et al. [17] studied the PZ/MDEA equilibrium at pressure nearing 5 MPa. Similar results were presented by groups of Bottinger [18] and Bottger [19] for high pressure equilibria of CO_2-PZ-MDEA solutions. A solitary dataset is reported by Silkenbaumer et al. for carbon dioxide absorption in AMP/MDEA mixtures [20]. Most notably, majority of the experimental points of carbon dioxide laden aqueous PZ/MDEA blends has been reported in low carbon dioxide pressure region and for low piperazine concentrations in MDEA. Since majority of data has been reported in low-pressure region, the experimental information cannot be effectively extrapolated to high pressure-region due to its highly non-linear nature [21]. Hence, experimental studies of carbon dioxide solubility in alkanolamine blends in the high gas loading region is important in development of MDEA based blended solvents for high-pressure carbon dioxide capture systems.

In this study, the experimental solubility of carbon dioxide was determined in equimolar concentrations (1 + 1 M and 2 + 2 M) of separate blends of N-methyldiethanolamine with piperazine and 2-

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amino-2-methyl-1-propanol. The studies were performed at a moderate range of temperature (303.15–343.15K) and pressure (102.5–4110 kPa). A neural network based analysis [22] was carried out to compare our findings with the literature. Moreover, experimental findings of this study and those in open literature were satisfactorily correlated by a hybrid Kent–Eisenberg (KE) model [23].

2. Materials and methods

All chemicals used in this study were purchased from Merck Malaysia (Pvt.) Ltd (Kuala Lumpur, Malaysia) and were of used without further purification. Gas Walker (Pvt.) Ltd (Kuala Lumpur, Malaysia) provided carbon dioxide gas and nitrogen gas. Detailed information on materials used in this study is listed in Table 1. A Sartorius BSA224S-CW mass balance (Sartorius Stedim Malaysia, Kuala Lumpur, Malaysia ($u = 0.1$ mg) was used to prepare separate 1 and 2 M aqueous solutions of AMP, PZ and MDEA in deionized water at 298.15K.

The high-pressure vapor-liquid equilibrium (HP-VLE) apparatus, shown in Fig. 1, was used to experimentally measure the solubilities of carbon dioxide in alkanolamine blends. Detailed information about the equipment is available in our previous publication [24]. The reliability of the equipment was ascertained by replicating selective carbon dioxide solubility in single aqueous MDEA and PZ solutions, found in open literature. The reiterated values are presented in Table 2.

In a typical run, carbon dioxide gas was filled in the feed cell, up to 5000 kPa by opening valve V1 and allowed to equilibrate for 2 h at 303.15K. 100 ml of freshly prepared and degassed alkanolamine solution was filled in the solubility cell and flushed with nitrogen gas. The solubility cell was heated to the desired temperature and carbon dioxide gas was slowly transferred. Hence, the moles of carbon dioxide gas transferred to the solubility cell, n_{fed}, were calculated by equation (1).

$$n_{fed} = n_1 - n_2 \tag{1}$$

where n_1 and n_2 are the moles of carbon dioxide in the feed cell, before and after the gas was transferred to the solubility cell. Both values were calculated by the Span and Wagner equation of state using the subsequent pressure and temperature readings in the feed cell [27].

The pressure of carbon dioxide in the solubility cell dropped with time as the gas dissolved in the aqueous alkanolamine blend. After, the pressure in the solubility cell stabilized for at least an hour, the pressure and temperature readings at the equilibrium were recorded and the contents of the solubility cell were discarded. The partial pressure of carbon dioxide at equilibrium, P_{CO2}, was determined using equation (2).

$$P_{CO2} = P_T - P_N - P_W - P_A \tag{2}$$

where P_N, P_W and P_A are the partial pressures of nitrogen, water and alkanolamine in the solubility cell under equilibrium conditions, respectively and determined using a method based upon Dalton's law of partial pressure, given by Refs. [24,28]. P_T is defined as the total pressure in the solubility cell at equilibrium. The CO_2 loadings were determined by equation (3).

$$\alpha = \frac{n_{abs}}{n_{alk}} \tag{3}$$

where n_{alk} and n_{abs} is the moles of alkanolamine blend in the solubility cell initially and carbon dioxide absorbed. The latter is calculated by equation (4).

$$n_{abs} = n_{fed} - n_{res} \tag{4}$$

where n_{res}, is the residual moles of CO_2 in the solubility cell at equilibrium.

3. Thermodynamic framework

A recently developed hybrid Kent-Eisenberg model [23] was extended to the correlation of experimental solubility of alkanolamine mixtures, by incorporation of equilibrium model equation developed for alkanolamine blends in another publications [29,30]. The reaction mechanisms of carbon dioxide with aqueous AMP, MDEA and PZ solutions are generally written as in equations (5)–(9) [29].

$$RRNH_2^+ \xrightleftharpoons{k_a} RRNH + H^+ \tag{5}$$

$$MDEAH^+ \xrightleftharpoons{k_b} MDEA + H^+ \tag{6}$$

$$H_2O + CO_2 \xrightleftharpoons{k_c} H^+ + HCO_3^- \tag{7}$$

$$HCO_3^- \xrightleftharpoons{k_d} H^+ + CO_3^{-2} \tag{8}$$

$$H_2O \xrightleftharpoons{k_e} H^+ + OH^- \tag{9}$$

The equilibrium constants, k_a-k_e for the above equation are provided below.

$$k_a = \frac{[RRNH][H^+]}{\left[RRNH_2^+\right]}, k_b = \frac{[MDEA][H^+]}{[MDEAH^+]}, k_c = \frac{\left[HCO_3^-\right][H^+]}{[CO_2]}, k_d = \frac{\left[CO_3^{-2}\right][H^+]}{\left[HCO_3^-\right]}, k_e = \left[OH^-\right]\left[H^+\right]$$

where $RRNH$ and $RRNH_2^+$ represents PZ/AMP free and protonated concentrations, respectively.

The amine balance for the said system is given in equations (10) and (11).

Table 1
Sample provenance table.

Materials	Abbreviation	CAS	Purity	Source	Purification Method
2-amino-2-methyl-1-propanol	AMP	124-68-5	0.982 (mass fraction)	Merck Malaysia (Pvt.) Ltd.	none
N-methyldiethanolamine	MDEA	105-59-9	0.990 (mass fraction)	Merck Malaysia (Pvt.) Ltd.	none
Piperazine	PZ	110-85-0	0.995 (mass fraction)	Merck Malaysia (Pvt.) Ltd.	none
Carbon dioxide	CO_2	124-38-9	0.999 (volume fraction)	Gas Walker (Pvt.) Ltd.	none
Nitrogen	N_2	7727-37-9	0.999 (volume fraction)	Gas Walker (Pvt.) Ltd.	none