

Solubility of heptane in aqueous solutions of methyldiethanolamine (MDEA)



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ARTICLE INFO

Article history:

Received 15 November 2015

Received in revised form

20 January 2016

Accepted 21 January 2016

Available online 22 January 2016

Keywords:

Thermodynamic equilibrium

MDEA

Heptane

Solubility

Gas sweetening

ABSTRACT

New experimental solubility data of heptane in aqueous amine solutions is presented. Simple equilibrium cells were used to measure the solubility of heptane in aqueous amine systems in the range: 298–328 K. Aqueous liquid samples were analyzed using a gas chromatograph. It was observed that heptane solubility in Methyldiethanolamine (MDEA) solutions increased with increasing temperature. Also, increasing amine concentration in the tested solution, the solubility of heptane increased. Simple models were developed in order to represent the activity coefficient of heptane in the aqueous MDEA solution in the range of 40–50 wt % MDEA. The Henry's law-based model allowed for a more direct comparison between the solubilities in pure water and in the aqueous solution of MDEA. The obtained heptane solubility data were compared to predicted data using group contribution equation of state model (GCA-EoS).

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1. Introduction

Methyldiethanolamine (MDEA) and alkanolamine solutions are generally used in gas sweetening process to strip acid gases, specifically carbon dioxide (CO₂) and hydrogen sulfide (H₂S). Alkanolamine solutions are highly selective towards absorption of these acid gases [1]. The acid gases are considered as corrosive agents. The existence of acid gases with liquid water in the process vessels and pipes threatens their structures from corrosion. Hence, they should be removed and their concentrations kept below the design specification of 4–20 ppm H₂S and less than 3% CO₂ [2].

One of the advantages of using alkanolamines solutions is that they dissolve selectively more acid gases than hydrocarbons. Hydrocarbons have low solubility in alkanolamines solutions. This low solubility however represents lost product in natural gas treating solvents. The solubility of light alkanes and BTEX in aqueous MDEA and other alkanolamine were investigated by several researchers [3–11]. Indeed, hydrocarbons losses are more significant for light hydrocarbon i.e. methane (C1), ethane (C2), propane (C3) and butane (C4) than heavy liquid hydrocarbon i.e. pentane (C5), hexane (C6) and heptane (C7). Most of the available data in literature focused on light hydrocarbon solubility [2–5]. Nevertheless, the

solubility profile for heavy hydrocarbon is of high importance not just to determine the magnitude of hydrocarbons losses but also for their influence on alkanolamines foaming.

Foaming during gas sweetening is one of the major operational problems. It can be induced by various contaminants including liquid hydrocarbon [12]. Foaming normally leads to serious consequences such as loss of absorption capacity, reduced mass transfer area and efficiency and carryover of amine solution to the downstream plant [13]. Foamed alkanolamines may carry large amounts of hydrocarbons contributing to hydrocarbons losses, which far exceeds that expected from solubility alone [14]. Complications of foaming is enhanced when the solution has sufficient liquid organic capable of increasing the solution viscosity and density and reducing the solution surface tension [12].

This study arise as a part of the ongoing project studying the deterioration of solvent quality and foaming problem in Habshan Gas Sweetening Unit (HGSU) at Abu Dhabi Gas Industries Limited (GASCO) which is a natural gas producing company of Abu Dhabi, UAE. In GASCO 40–50 wt% MDEA is used for acid gas removal.

2. Modeling approach using Henry's low and activity coefficient

The following assumptions are considered valid in this modeling:

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- There is no significant amount of water or alkanolamine in the organic phase. This was confirmed by analyzing samples from the organic phase and considering works of other researchers [15–18].
- There is no significant amount of water or alkanolamine in the vapor phase, since the organic phase is in direct contact with the vapor phase [1,15–18].

Henry's law can be used to model the solubility of heptane in aqueous MDEA solution [14,19,20]. The presence of amines in the aqueous phase increases hydrocarbon solubility over that in water, an effect referred to as "salting-in" [14].

Thermodynamics of the studied system based on activity coefficient model was described in details at our recent publication [21]. Due to very low mutual solubilities in aqueous solvent–hydrocarbon systems, it was very easy to reach vapor–liquid–liquid equilibrium (VLLE) conditions [5,6]. Thus, it can be assumed that the organic phase was composed mainly of heptane, while the aqueous phase mainly comprised of water and MDEA. Similar assumptions were followed by Valtz et al. [5–7,9] for modeling the solubility of aromatics in amine solutions.

The equilibrium between the aqueous phase and the heptane phase can be expressed by

$$X_{\text{Heptane}}^o \gamma_{\text{Heptane}}^o = X_{\text{Heptane}}^{aq} \gamma_{\text{Heptane}}^{aq} \quad (1)$$

where; $\gamma_{\text{Heptane}}^{aq}$ and $\gamma_{\text{Heptane}}^o$ are activity coefficients of hydrocarbon species, in the aqueous and hydrocarbon rich liquid phase, respectively.

Since the hydrocarbon phase was assumed to be pure heptane, the following relations hold:

$$X_{\text{Heptane}}^{aq} \gamma_{\text{Heptane}}^{aq} = 1 \quad (2)$$

$$\gamma_{\text{Heptane}}^{aq} = \frac{1}{X_{\text{Heptane}}^{aq}} \quad (3)$$

The aqueous phase could be modeled by Henry's law or/and the activity coefficient model, as following:

$$x_i H_i(T) = x_i^{aq} \gamma_i^{aq} f_i^{sat} = 1 \times f_i^{sat} \quad (4)$$

The liquid fugacity of the pure hydrocarbon could be approximated as follows:

$$f_i^{sat} = \phi_i^{sat} \times P_i^{sat} \quad (5)$$

Then,

$$x_{iw}^* H_{iw}(T) = \phi_i^{sat} \times P_i^{sat} \quad (6)$$

Henry's constant for water-hydrocarbons system could be calculated by Eq. (7) below.

$$\ln H_w = A + \frac{B}{T} + \text{Cl} \ln T \quad (7)$$

The effect of alkanolamine on the solubility of heptane was modeled using the salting-in ratio (S_{ia}). Henry's constant for heptane in aqueous amine solution (H_{ia}) was calculated using the salting-in ratio:

$$S_{ia} = \frac{H_{iw}}{H_{ia}} = \frac{x_{ia}}{x_{iw}} \quad (8)$$

3. Experimental procedure for n-heptane solubility measurements

3.1. Apparatus and experimental procedures

Simple equilibrium cells immersed in an oil bath at fixed temperature in range of 298–328 K were used to study thermodynamic equilibrium. Fig. 1 shows a schematic of the experimental cell.

The origin and purity of used chemicals are reported in Table 1.

Three MDEA concentrations, i.e. 40, 45 and 50 wt % were prepared from commercial MDEA treating solvent provided by GASCO. The equilibrium cell was loaded with 25 mL of solvent (aqueous MDEA solution) and 15 mL heptane. Under this condition two liquid phases were present in the cell. The aqueous phase was stirred vigorously for a long time, more than 12 h to achieve phase equilibrium. Stirring was stopped for 1 h and samples of aqueous phase were withdrawn and analyzed by gas chromatography. Several samples from each experiment were analyzed to ensure the repeatability of the results. Random experiments were duplicated to test the reproducibility of the results. The standard uncertainty in the mole fraction of heptane based on the repeatability and reproducibility measurements were $\approx 3.10^{-06}$.

All analyses were performed in Agilent 6890 N Gas Chromatograph equipped with a Flame Ionization Detector. Chromatographic separation was accomplished with an HP-5, 30 m, 0.32 mm i.d., 0.25 μm film. Split injection mode was used and adjusted to achieve the best reproducibility. The best split ration was found to be 2%. The injection inlet temperature was adjusted to 250 °C. Fig. 2 depicts the used analytical circuit and Table 2 tabulates the thermal programming followed in the GC analysis.

In order to avoid or reduce the possibility of losing hydrocarbon due the split mode and adsorption throughout the column, a blank injection of the pure hydrocarbon was used frequently between samples measurements. For heptane, a calibration line was generated, as can be seen in Fig. 3.

The vapor phase was assumed to be pure heptane and thus the pressure in the equilibrium cell was the vapor pressure of pure heptane at each experimental temperature. Vapor pressure of pure heptane could be calculated from Wagner equation [22,23] or Antoine equation [24].

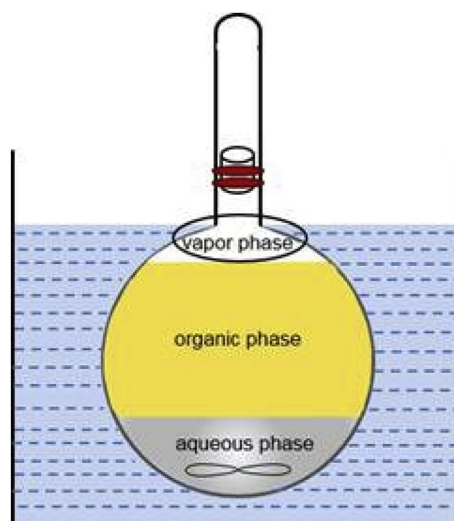


Fig. 1. Schematic diagram for the simple equilibrium cell [21].

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