Fluid Phase Equilibria 427 (2016) 539–548

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Modeling of gaseous hydrocarbons solubility in aqueous-amine systems by VTPR model

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ARTICLE INFO

Article history:
Received 16 May 2016
Received in revised form
9 August 2016
Accepted 11 August 2016
Available online 13 August 2016

Keywords:
Alkanolamines
Light hydrocarbons
Gas solubility
VTPR model

ABSTRACT

It is crucial to know the solubility of gaseous and liquid hydrocarbons in aqueous alkanolamine solutions in order to quantify accurately the hydrocarbon losses in treating processes. Hence, consistent experimental data and accurate models are essential for the efficient design and optimization of these processes. In this work, a homogeneous approach based on the modified Volume Translation Peng-Robinson (VTPR) cubic equation of state was adopted to represent the solubility of methane, ethane and propane in aqueous mono-ethanol-amine, di-ethanol-amine and methyl-di-ethanol-amine which are the most common solvents used in the effluent treatment processes. The model parameters were estimated on the basis of binary and ternary vapor-liquid and liquid-liquid equilibrium data. The model developed shows a satisfactory representation of the experimental data with average deviations ranging from 1 to 28% for all systems, and gives a solid foundation for predicting hydrocarbon solubility in aqueous alkanolamine solutions.

1. Introduction

Sweetening of natural gas and liquefied petroleum gas (LPG), using amine aqueous solutions for the removal of contaminants such as CO_2, H_2S, COS/CS_2, NH_3, mercaptans, BTEX and all other unusual impurities, is one of the most important purification processes encountered in the petroleum industry prior to the product sale. Purification of the hydrocarbon streams may generate some losses of the hydrocarbon compounds into the absorbent solution streams. Knowing the amount of the hydrocarbons absorbed by the amine solutions (solubility) has a significant positive effect on the design and control of the amine sweetening facilities.

Most of the reviews available in the literature give attention to the equilibrium or solubility concerning acid gases contaminant in amine aqueous solutions since the objective is primarily to maximize the efficiency of the absorption process. However, since the presence of hydrocarbon in amine solution may create some problems in downstream processes and/or lead to unwanted atmospheric emissions, hydrocarbon solubility data determination has received more attention by the various stakeholders in the petroleum field. Thus, several studies have investigated the hydrocarbon-aqueous amine systems in order to control and improve the overall efficiency of the hydrocarbon treatment process. Most of them provide experimental solubility data for the main components of the natural gas and LPG's, namely, methane, ethane, propane, n-butane, n-pentane and n-hexane in different aqueous amine solutions. Other works include the solubility of unhealthy aromatic hydrocarbon compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX) as they are part of the hydrocarbon streams to be purified. In those studies, the most common amine treatment solvents considered are: Mono-Ethanol-amine (MEA), Di-Ethanol-amine (DEA), Tri-Ethanol-amine (TEA), Methyl-Di-Ethanol-amine (MDEA), Di-Glycol-amine (DGA) and Di-Iso-Propanol-amine (DIPA), comprising primary, secondary and tertiary amines.

In this study, particular focus will be given to the main

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http://dx.doi.org/10.1016/j.fluid.2016.08.018

components of natural gas, namely, methane, ethane and propane and their solubility in MEA, DEA and MDEA solutions. A summary of the existing experimental data, for systems including methane, ethane and propane, along with the various operating conditions is presented in Table 1.

As can be seen from Table 1, methane-alkanolamines and ethane-alkanolamines are the most investigated systems mostly at vapor-liquid equilibrium (VLE) conditions. Then, propane-alkanolamines systems follow with different equilibrium conditions (VLE, LLE, and VLLE). Furthermore, most authors treated the solubility in three amine solvents, namely, MEA, DEA and MDEA at a concentration of 3 kmol/m^3, and that is to reproduce the same conditions commonly found in the industrial treatment processes. The solubility in DIPA has been exclusively studied by Critchfield et al. [7] except for propane with the data of Jou et al. [14]. The solubility data in TEA solutions have been produced only for methane [5] and ethane [10]. Recently, Mokraoui et al. [12] have given a new supplementary data series for ethane and propane, in DEA and MDEA aqueous solutions and at VLLE conditions in order to cover the need for industrial LPG treating units. In the other hand, by exploring the set of data sources presented in Table 1, it is possible to draw some general features related to hydrocarbon – aqueous amine systems as revealed by several authors [7,15,16]. The first statement is that the higher is the concentration of amine in the aqueous solution the higher is the solubility of the hydrocarbons. The second is that the lighter hydrocarbons are more soluble in amines than the heavier ones, which is a direct consequence of the molecular weight effect. Finally, the amine solubility capacity with respect to hydrocarbons is: MEA < DEA < DGA < MDEA < DIPA.

2. Modeling of ternary hydrocarbons aqueous alkanolamine systems

Like water-hydrocarbon systems, reliable knowledge of solubility and vapor-liquid equilibrium of hydrocarbons aqueous amine solutions over a wide range of temperatures and pressures is essential for designing the most efficient industrial operations of petroleum processes. As the hydrocarbons are sparingly soluble in the aqueous amine solvents, the thermodynamic modeling of the solubility was rather handled based on an heterogeneous approach (gamma-phi approach), usually applied to systems with dissimilar compounds involving non-polar and polar molecules such as hydrocarbons and amines, respectively. Hence, earlier works, treating the solubility modeling of hydrocarbons in amines, used the traditional Henry's Law approach, which is often suitable for systems having very low solubilities of gases in the liquid solvent. The basis for this approach is to start with the solubility of hydrocarbons in water, since water makes up at least 85 mol % of most treating amine solutions. Then, the presence of amine is characterized by the Salting-in effect, which indicates the increase of solubility due to the higher affinity of hydrocarbons towards amines compared to water. Hence, using this approach, the solubility of hydrocarbons in amine treating solvent is determined using two temperature-dependent parameters: the Henry's law constant of hydrocarbons in pure water, H^o and the Setschenow coefficients S, which accounts for the Salting-in effect, [17,18].

In line to this approach, Carroll and Mather [19] presented a model to correlate the solubility of methane, ethane and propane in pure water and aqueous alkanolamines. The model considered the general case in which three phases may coexist: a vapor phase, a hydrocarbon rich phase and an aqueous amine-rich liquid phase. The authors used a Henry's law for the aqueous phase and a Peng-Robinson equation of state for both vapor and non-aqueous liquid phase. The obtained results showed a relatively satisfactory agreement between calculated and experimental data for both hydrocarbon – water and hydrocarbon – aqueous alkanolamines systems although significant deviations have been perceived for some sets of data.

Similarly, Bullin and Brown [20] from Bryan Research & Engineering Inc. (BR&E) have presented and published in conference proceedings a consistent method to predict and control absorption/desorption of HC in amine sweetening units. Using the available VLE and operating plant data from different sources, BR&E developed a model based on Henry's Law approach for the solubility calculation of HC and BTEX in amine solutions. This model has also been integrated into a software package of industrial nature named ProMax [21]. The software also incorporates more complete thermodynamic models with extended set of equations of state and activity coefficient models to handle more amine compounds in presence of acid gas in order to simulate a more complex amine sweetening facilities.

Table 1
Reported experimental solubility data for methane, ethane and propane in different aqueous alkanolamine solutions.

Year	Authors	Solvent	Concentrations	Temperature range (°C)	Equilibrium
Methane in amine solutions					
1976	Lawson and Garst [1]	MEA, DEA	5, 15, 25, 40 (wt%)	37.8–121	VLE
1986	Dingman [2]	DGA	50 (wt %)	65.6–87.8	VLE
1998	Jou et *al.* [3]	DGA	3, 6 (M)	25–125	VLE
1998	Jou et *al.* [4]	MDEA	3 (M)	25–130	VLE
1998	Carroll et *al.* [5]	MEA, DEA, TEA	3 (M)	25–125	VLE
2001	Addicks et *al.* [6]	MDEA	–	40, 80	VLE
2001	Critchfield et *al.* [7]	MEA, DEA, DGA, MDEA, DIPA	3, 4.5 (M)	40	VLE
2002	Addicks et *al.* [8]	MDEA	30 - 50 (wt%)	40–80	VLE
2006	Jou and Mather [9]	MDEA	100 (wt%)	25–130	VLE
Ethane in amine solutions					
1976	Lawson and Garst [1]	MEA, DEA	5, 15, 25, 40 (wt%)	37.8–121	VLE
1996	Jou et *al.* [10]	TEA	2, 3, 5 (M)	25–150	VLE
1998	Jou et *al.* [4]	MDEA	3 (M)	25–130	VLE
2001	Critchfield et *al.* [7]	MEA, DEA, DGA, MDEA, DIPA	3, 4.5 (M)	40	VLE
2006	Jou and Mather [11]	MEA, DEA	3 (M)	25–125	VLE, VLLE
2013	Mokraoui et *al.* [12]	MDEA, DEA	25, 35, 50 (wt%)	10–30	VLE, VLLE
Propane in amine solutions					
1992	Carroll et *al.* [13]	MDEA	3 (M)	0–150	VLE, VLLE, LLE
2001	Critchfield et *al.* [7]	MEA, DEA, DGA, MDEA, DIPA	3, 4.5 (M)	40	LLE
2002	Jou et *al.* [14]	MEA, DEA, DGA, MDEA, DIPA	0.7–16.5	40–75	LLE
2013	Mokraoui et *al.* [12]	MDEA, DEA	25, 35, 50 (wt%)	25–60	VLE, VLLE