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Surrogate Model for Carbon Dioxide Equilibrium Absorption Using Aqueous Monoethanolamine

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A novel surrogate model useful for designing CO_2 absorption columns is provided to describe the vapour-liquid equilibrium of CO_2 in a flue gas or biogas and aqueous monoethanolamine (MEA). The surrogate model is adjusted with experimental data and compared with dedicated software for electrolyte mixtures, i.e. OLI®. The assessment of CO_2 partial pressure is conducted at different MEA concentrations, temperatures and loading of CO_2/ MEA in the liquid phase. The OLI® model is in good agreement with the experimental data when MEA concentration is between 15 to 30 % wt, as well as for high MEA concentrations (between 45 and 60 % wt) at 60 °C. However, for temperatures above 80 °C, the model is in agreement with experimental data only when the load of CO_2 in the liquid phase exceeds the range from 0.25 to 0.30 (usual industrial operating range is from 0.2 to 0.4). A point not addressed in experimental data in literature is the presence of MEA in the vapour phase, which overcomes the recommended values from health safety point of view at 100 °C. The presence of MEA in biogas could produce NOx. The influence of inert gas (CH_4) on the equilibrium is considered to check the model suitability for biogas enrichment. The novel surrogate model provides a good regression of all the experimental data in the operating region and it is validated using Pareto diagrams.

1. Introduction

The most extended and mature option for carbon dioxide capture is the chemical absorption with monoethanolamine (MEA) (Lang et al., 2017). The physical absorptions are modelled using Henry's law but nowadays there is no simple model useful for chemical absorption which relates the equilibrium concentration of a component in the gas and in the liquid. Scrubbing effluent industrial fluid streams of acid gases such as CO_2 and H_2S is applied for various reasons such as improving the calorific value of biogas streams and avoiding corrosion in process lines and fittings. Recently, a more compelling reason for scrubbing of CO_2 from process streams is the urgent need to reduce greenhouse gas emissions. The main cause that the pilot plant results do not fit previous simulations is the thermodynamic model, therefore a reliable equilibrium model for carbon chemical absorption is of great importance. The models nowadays take into account the multiple reactions that take place in the liquid phase (Madeddu et al., 2017). Simulation and optimization of carbon dioxide-MEA absorption units are out of the scope of the present study and can be found in literature, e.g. Wang (2017).

Several studies have been carried out on the solubility of CO_2 in aqueous MEA solution. Tables presenting summaries of previous studies were presented by Kohl and Nielsen (1997) and updated by Ma'mun et al. (2005). Additionally, the experimental data tables of Jou et al. (1995) cover a wide range of temperatures, pressures and loadings, although being available only for 30 mass % MEA. The behaviour of vapour-liquid equilibrium of CO_2-H_2O-MEA mainly depends on the concentration of MEA and the conditions of temperature and pressure at which the system is operated.

The load of CO_2 in the liquid (α) represents the ratio of moles of aqueous CO_2 and moles of aqueous MEA, both in their different ionic forms. In the industrial processes of CO_2 absorption with MEA, the usual α operating range

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is between 0.2 and 0.4 (Luo et al., 2015). The industrial interest is to design absorption columns in the mentioned range of CO_2 load**.**

2. Methodology

The surrogate model is performed using multilinear regression using Microsoft Excel®. The determination of the partial pressure of CO_2 at different concentrations of MEA, temperatures and loading of CO_2/ MEA in the liquid is conducted. The simulation of the CO_2 absorption using aqueous MEA is performed using OLI® software. The simulations were performed according to the studied ranges in the literature, i.e. from 15 to 60 % of MEA and temperatures from 40 °C to 120 °C. On the other hand, an assessment of the influence on the equilibrium in the presence of an inert gas like methane (CH_4) instead of CO_2 is performed to check that CH_4 does not affect the equilibrium and the model is valid for biogas enrichment. For pressures from 0.03 to 300 atm the simulation can be conducted using pure CO_2, but the presence of CH_4 is a good option to simulate the conditions with a very low partial pressure of CO_2 keeping the overall pressure at 1 atm. A large amount of liquid phase versus vapour phase is used to ensure that the equilibrium composition of the liquid does not change too much with respect to the initial condition, e.g. 1000 kg of water/MEA for 50 kg of CH_4. The loss of MEA in the vapour phase is a parameter of significant importance from the environmental point of view but, unfortunately, there is no experimental data available in this respect. Therefore, this point is also considered in the present study, using OLI® software.

3. Surrogate model

The adjustment is obtained by a novel equation (Eq. 1) that in our knowledge has not been previously proposed in the literature, in which temperature is represented in K, and the constant of ideal gas R is 8.314 $m^3 \cdot$ Pa/K/mol. This equation is obtained from the multilinear regression of literature experimental data with loads between 0.2 and 0.4. With this equation, the natural logarithm of the CO_2 partial pressure, in Pa, is calculated.

$$LnPCO_2 = 32.95 + 14.96 \cdot (\alpha) - 88{,}081 \cdot \left(\frac{1}{RT}\right) \qquad (1)$$

4. Results

Figures 1, 2, 3 and 4 illustrate the partial pressure of CO_2 for various concentrations of MEA solutions (15, 30, 45 and 60 % wt), allowing the comparison of profiles resulting from experimental data, OLI® simulation and surrogate model, respectively. The values obtained by OLI® are generally in agreement with experimental data. The surrogate model fits very well the experimental data in the range of CO_2 operating load from 0.2 to 0.4. The novel surrogate model fits the experimental data even better than OLI® in some conditions for these mentioned operating loads. OLI® overestimates the partial pressure of CO_2 at 120 ºC, low loads (0.2) and 15 % or 30 % wt MEA (Figures 1e and 2e respectively) and at temperatures above 80 °C and 45 % or 60 % wt MEA (Figures 3c, d, e and 4c, d, e respectively). At 60 % wt MEA and temperatures between 40 and 60°C, OLI® overestimates the experimental data at high loads and OLI® underestimates it at low loads (Figures 4 a, b). At 30 % wt MEA and 120°C (Figure 2e), OLI® values fit better to Jou et al. (1995) experimental data than to the results of other authors. However, the parity plot between experimental data and OLI® simulations shows a good agreement for the CO_2 partial pressure for any operating load (Figure 5a). Although the surrogated model simplicity and its fitting for the range of operating load from 0.2 to 0.4, it is able to extrapolate quite well for other loads as shown in its Pareto diagram (Figure 5b). It is also important to notice that the experimental data is also subject to experimental error and the experimental data is under or overestimated by the regressed model depending on the authors that generate them. For instance, the CO_2 partial pressure data of Aronu et al. (2011) is in general underestimated by the model, while the data of Jou et al. (1995) and Wagner et al. (2013) are generally overestimated.

According to the proposed model, the CO_2 partial pressure depends on the load and temperature; therefore, different % MEA concentration curves should match at a constant temperature. Figure 6 shows the concentration dependency of CO_2 partial pressure for the H_2O–MEA–CO_2 system as determined by experimental data in literature of Aronu et al. (2011) and the surrogated model. The load versus the natural logarithm of partial pressure presents a sigmoidal shape. This sigmoidal shape motivates that the loading CO_2 is operated in the range of 0.2 to 0.4, since in this range the lowest slope is presented, e.g. to work at a higher load than 0.4 then a significant increase in pressure is required to obtain a slight increase of CO_2 load. A good agreement is obtained with the surrogated model and the middle zone of the sigmoidal curve.

The amount of MEA lost in the vapours is an important parameter from costs and environmental point of view, e.g. biogas combustion could produce NOx. Figure 7 shows the vapour pressure of MEA obtained by 30 % wt. solutions of MEA, which is the MEA concentration most industrially used. The filled circles show the partial pressure of MEA in the absence of inert gases and each temperature is represented by a distinct colour. In the absence of an inert gas, when the load of CO_2 tends to zero, the curves converge to the same partial pressure of MEA regardless of the temperature. There is a specific load, function of temperature that minimizes the partial pressure of MEA. At lower operating temperatures, the partial pressure of MEA is less and the minimum is reached at a higher load. At 100 °C, the partial pressure of MEA in the vapours is above 6 ppm (threshold limit value), although the system is pressurized to 10 bar. For low loads, in the presence of an inert gas, the vapour partial pressure of MEA decreases and fails to converge to the common value indicated above. Figure 8 shows the influence of the % MEA in aqueous solution. The same behaviour described for 30 % MEA is also valid for other concentrations. The higher the concentration of MEA present in the mixture, the higher is its amount in the vapour phase

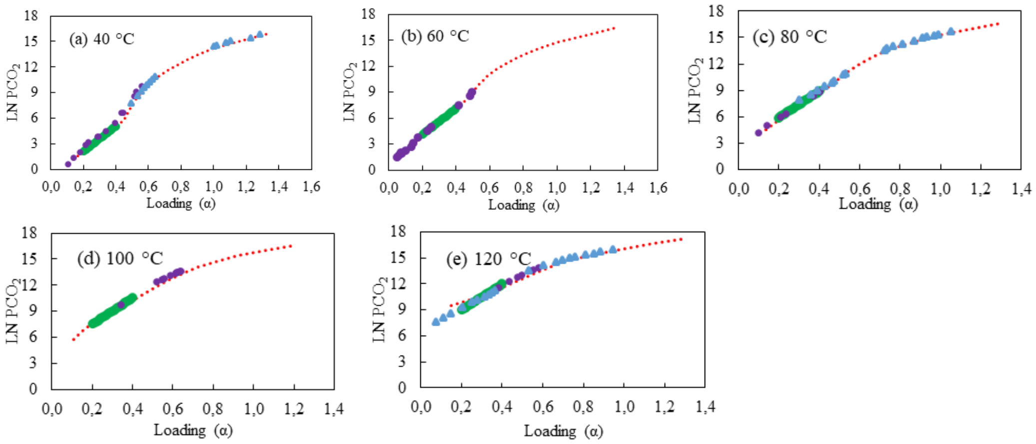

Figure 1: Logarithm of the CO_2 partial pressure function of the CO_2 load in liquid into 15 mass% MEA. Experimental data in literature: circle, Wagner et al. (2013); triangle, Aronu et al. (2011); dotted line, OLI®; Line —, Proposed model.

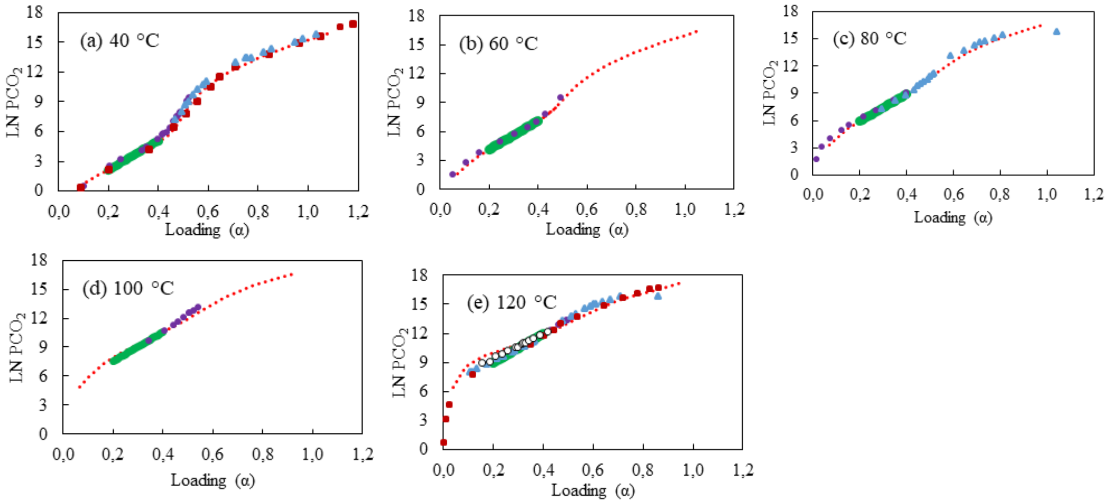

Figure 2: Logarithm of the partial pressure of CO_2 a function of the load of CO_2 in the liquid into 30 mass % MEA. Experimental data in literature: squares, Jou et al. (1995); empty circles, Ma'mun et al. (2005); triangles, Wagner et al. (2013); full circles, Aronu et al. (2011); dotted line, OLI®; Line —, Proposed model.

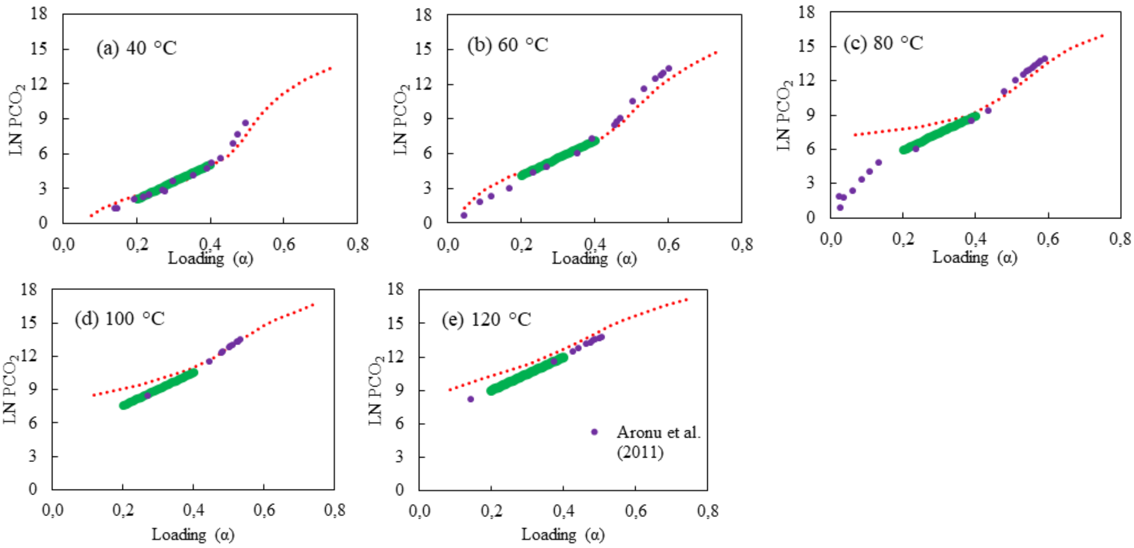

Figure 3: Logarithm of the partial pressure of CO_2 a function of the load of CO_2 in the liquid into 45 mass % MEA. Experimental data in literature: ●, Aronu et al. (2011); dotted line, OLI®; Line –, Proposed model.

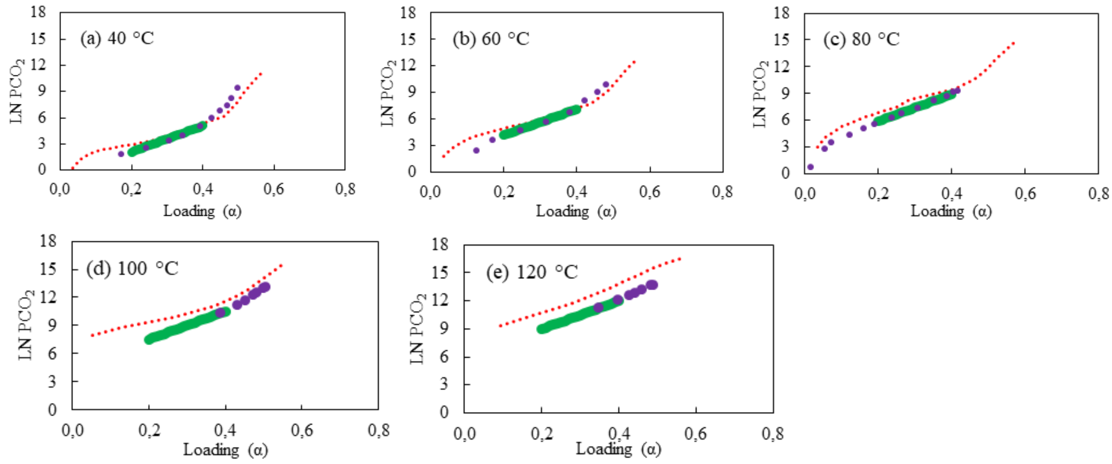

Figure 4: Logarithm of the partial pressure of CO2 a function of the load of CO_2 in the liquid into 60 mass % MEA. Experimental data in literature: ●, Aronu et al. (2011); dotted line, OLI®; Line –, Proposed model.

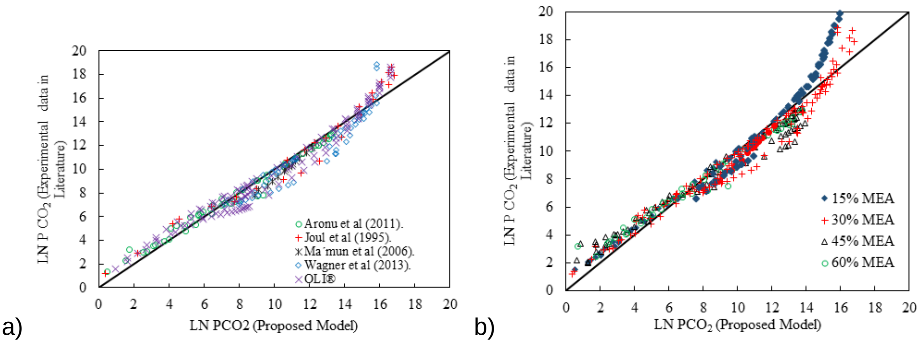

Figure 5: Parity plot between experimental literature and: (a) OLI®, (b) surrogated model

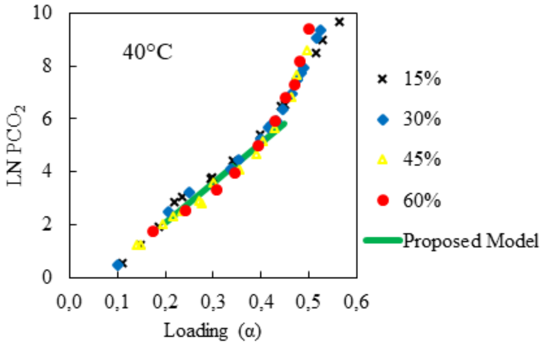

Figure 6: Concentration dependency of equilibrium CO_2 partial pressure of the H_2O-MEA-CO_2 system at 40°C for different concentrations of % wt MEA.

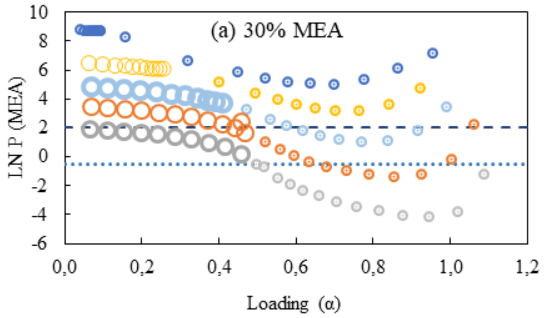

Figure 7: MEA Vapours Pressure 30% MEA. Temperatures from bottoms to top curves: 40°C; 60°C; 80°C; 100°C; 120°C; threshold limit value at 1 bar (dotted line) and 10 bar (discontinuous line)

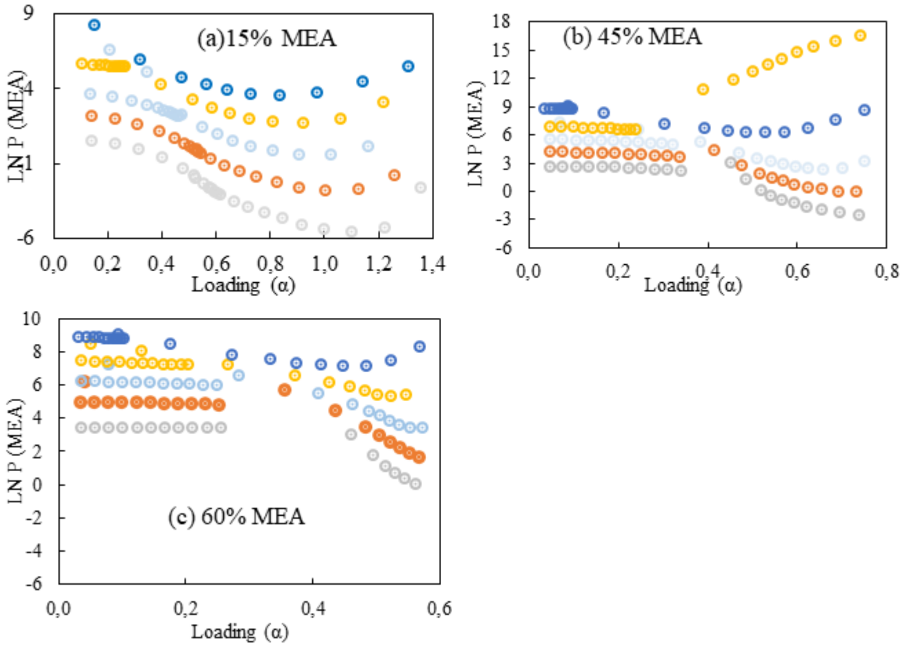

Figure 8: MEA Vapours Pressure at 15, 45 and 60 % MEA. Temperatures from bottoms to top curves: 40 °C; 60 °C; 80 °C; 100 °C; 120 °C.

5. Conclusions

Chemical absorption of CO_2 with MEA is widely used in the industry but, at the contrary of the physical absorption, there is not a simple model able to represent the CO_2 equilibrium between the liquid and the vapour phase. Results from dedicated simulation software to electrolyte systems such as OLI® are in good agreement with experimental data but require a complex model that was implemented by the software developers for each compound in its database. A simple surrogated model based on experimental data to determine the vapour pressure of CO_2 in equilibrium has been proposed, which depends only on the load and temperature. Even with its simplicity, it is in a very good agreement with experimental data in the usual operating conditions and a rather good agreement for a wide range of operating conditions. The surrogated model assumes that for a fixed temperature, the logarithm of the partial pressure of carbon dioxide is proportional to the load. This fact is true for the usual operating conditions but for loads higher than 0.4 a sudden increase of the slope is observed. This suggests that a larger pressure increase is required to obtain a smaller increase of CO_2 load. Hence, as it is not a desirable scenario, loads higher than 0.4 are not industrially used. Despite the small amount of MEA in the vapours, its concentration is above the recommended values from a safety point of view, at a temperature of 100 °C.

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