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Prediction of N₂O solubility in alkanolamine solutions from the excess volume property

Ardi Hartono, Emmanuel O. Mba, and Hallvard F. Svendsen*

Norwegian University of Science and Technology, 7491 Trondheim, Norway

Abstract

The CO₂ solubility is very important property when establishing thermodynamic models for the VLE. In order to obtain the CO₂ solubility the normal procedure is to use the N₂O analogy as the CO₂ solubility cannot be directly measured. This calls for a rather extensive experimental program. In this work a simple and less laborious model was developed based on the excess molar volumes to estimate the excess Henry's constant. This method only requires density data and the N₂O solubility into pure solvents (Water/ Alkanolamine). The model works well to represent experimental data for different temperatures and concentrations.

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1. Introduction

Measurement of the physical CO₂ solubility in aqueous alkanolamines at various concentrations and temperatures is very important for developing kinetic models and also for correct implementation of a thermodynamic description. It is not possible to measure the physical solubility of CO₂ in the absorbent solutions directly due to the reactive nature of any

* Corresponding author. Tel.: +47 735 94 100; fax: +47 73 59 40 80.
E-mail address: hallvard.svendsen@chemeng.ntnu.no.

absorbent with CO₂. Thus the term of ‘N₂O Analogy’ was introduced and has become very important for estimating the physical CO₂ solubility. Several studies have focused in the N₂O analogy [1-5], and although different correlations were proposed this method is still very interesting and challenging to study. The accuracy of the measurements is very crucial because inconsistencies in the solubility data may contribute to inconsistent results for the reaction kinetics study. The kinetic rate constant is proportional to the square of the apparent Henry’s law constant, thus 10 % uncertainty in Henry’s constant can result in 20% uncertainty in the kinetic rate constant.

Different experimental techniques were proposed to measure free CO₂ concentrations, i.e.: pressure-drop measurements [1-5], volume-drop measurements [6] and high pressure VLE to measure P-T-x data [7]. These techniques produce very good data when comparing their internal uncertainty (<5%). However, when data for the same system obtained from two different techniques are compared, the discrepancy seems to be somewhat bigger than 10 %.

Wang’s model [8] is the most commonly used model for N₂O solubility into aqueous solutions and was developed by using an analogy to excess thermodynamic properties. The excess Henry’s law constant is calculated from the difference between this property measured in mixtures and in the pure solvents. In order to calculate the Henry’s law excess property of this model, quite laborious experiments of density and N₂O solubility are needed for different concentrations and temperatures.

In the previous work [3], the excess Henry’s law constant property was calculated from the excess volume, via the density measurements by assuming the excess Henry’s constant to be proportional to the excess volume. The results suggest that the model could be improved. The advantage of this model is that it requires only the N₂O solubility data for pure solvents and the density of solutions. Density data for alkanolamines can often easily be found in the literature and when it comes to uncertainty, all density data are in very good agreement (less than 0.5%), contrary to N₂O solubility data (more than 10%).

2. Modeling Part

2.1.1. Excess Molar volume

For a binary system the excess molar volume can be derived from density measurements according to:

$$V^E = (x_1 \cdot M_1 + x_2 \cdot M_2) / \rho_m - x_1 \cdot M_1 / \rho_1 - x_2 \cdot M_2 / \rho_2 \quad (1)$$

where V^E , M , x and ρ are the excess molar volume, molecular weight, mol fraction and density respectively, and the subscripts 1,2 and m denote H₂O, alkanolamine and mixture, respectively.

The Redlich-Kister model [9] is a semi empirical model and most widely used to correlate the excess molar volume as function of composition and temperature, according to Eq. 2:

$$V^E = x_1 \cdot x_2 \cdot \sum_{n=1} A_n \cdot (1 - 2 \cdot x_2)^{n-1} \quad (2)$$

where A_n is the Redlich-Kister Coefficient.

The Redlich-Kister coefficient is a polynomial temperature dependency and can be expressed as:

$$A_n = \sum_{n=1} a_n \cdot T^{n-1} \quad (3)$$

where a is a constant.

To get a good fit to the excess property experiment, this model requires a high degree polynomial, hence a large number of parameters needs to be fitted.

2.1.2. Excess Henry's Constant

The excess Henry's constant was developed by using an analogy to excess thermodynamic quantities which represents a deviation from ideality [8]. This is defined based on the Henry's constants in pure solvent (alkanolamine or H₂O) being assumed ideal, whereas the Henry's constants in the mixture were assumed real. The difference in Henry's law constant between real solution and ideal solution was regarded as an excess Henry's constant and was represented in normalized terms as:

$$H^E = \ln H_{1,m} - \sum_{i=2}^n \Phi_i \cdot \ln H_{1,i} \quad (4)$$

where H^E , Φ , H , m , 1 and i represent excess Henry's constant, volume fraction, Henry's constant, a mixture, N₂O, and alkanolamine/H₂O, respectively.

The volume fraction was used because excess property values based on volume were closer to zero than if mole fractions were used [10]. The excess Henry's law constant was calculated by:

$$H^E = -\frac{1}{2} \sum_{j=2}^n \sum_{\substack{i=2 \\ (i \neq j)}}^n \alpha_{ij} \cdot \Phi_i \cdot \Phi_j - \Lambda \quad (5)$$

where α , Λ , i/j are the binary interaction parameters, the ternary or higher interaction parameter and compound (Alkanolamine/H₂O) respectively. Usually only the binary interaction parameters are used and no general equation for the binary interaction is available. Based on their own work, an expression for the binary interaction as a temperature and concentration dependency was suggested as:

$$\alpha_{ij} = k_1 + k_2 \cdot t + k_3 \cdot t^2 + k_4 \cdot \Phi_3 \quad (6)$$

where k_i and t are parameter and temperature respectively.

2.1.3. N₂O solubility from an Excess Volume

As was mentioned previously, a quite laborious work covering many different concentrations and temperatures is required to correlate the excess Henry's constant and in the Redlich-Kister model [9], also a large number of parameters is required. In this work, we assumed macroscopically that an excess volume could be associated to a vacant space for the gas molecule to dissolve in, hence we proposed a correlation for the excess Henry's constant based on the calculated excess volume of solution as a function of composition and temperature, according to:

$$V^E = (k_1 + k_2 \cdot T + k_3 \cdot x_2 + k \cdot x_2^2) \cdot x_2 \cdot (1 - x_2) \quad (7)$$

In previous work [3], the excess Henry's constant was assumed to be proportional to the excess volume ($\psi = 1$) and the model predictions worked very well up to 60 wt % amine concentration. When more data at very high concentrations were included, the model was over-predicting the data and this suggests that the correction factor could be improved according to:

$$H^E = \psi \cdot V^E \quad \text{where} \quad \psi = \sqrt{1 - \Phi_2^2} \quad (8)$$

The predicted Henry's constant can be calculated as:

$$\ln H_{1,m} = H^E + \sum_{i=2}^n \Phi_i \cdot \ln H_{1,i} \quad (9)$$

3. Results and discussion

In this result section we demonstrate the model used for predicting N_2O solubility into aqueous MEA solutions. The density of aqueous MEA was reported [11] and the excess volume was calculated with Eq. 1. Fig. 1a shows the excess molar volume of aqueous MEA solutions at different compositions and temperatures. The excess molar volume seems nearly temperature independent for $0.9 < x < 0.4$ whereas the effect of temperature is more pronounced for $0.4 < x < 0.9$. The excess volume is modeled with Eq. 7 whereas the density data can be calculated back with Eq. 1 as seen in Fig. 1b. The model shows very good agreement with the experimental data as also shown in the parity plot (Fig. 1c). The parameters in Eq.7 can be written as:

$$V^E = (-1.9210 + 1.6792 \cdot 10^{-3} \cdot T - 3.0951 \cdot x_2 + 3.4412 \cdot x_2^2) \cdot x_2 \cdot (1 - x_2) \quad (10)$$

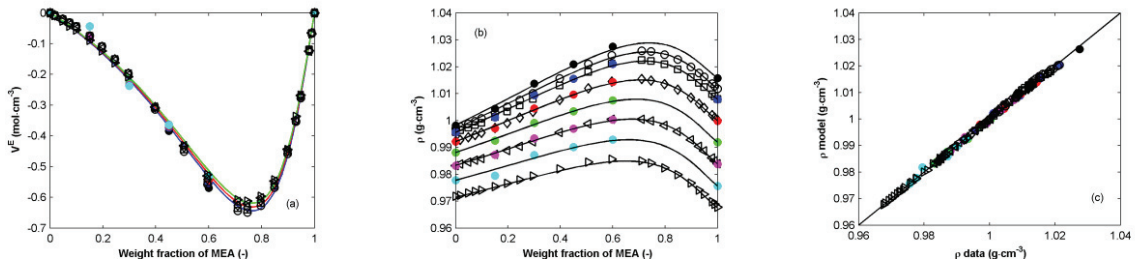


Figure 1. Model prediction for (a) Excess volume (\square , 20°C; \circ , 50°C; \triangle , 80°C; (b) Density of solution and (c) Parity plot for an aqueous solution MEA as a function of temperature and concentration (Unfilled points, [11]; Filled points, [3]).

Eq. 10 shows that only 4 parameters are needed to get a good representation of the data and this is less parameters than needed in the Redlich-Kister model.

The excess Henry's constant is often represented by the Wang model as calculated with Eq. 6. Different parameters were suggested based on the data used. Different suggested excess Henry's constants for aqueous MEA solutions as function of concentration are shown in Fig. 2. The three different excess Henry's constant models [8,12-13] seem very data dependent. It is seen that the three models behave differently and it is suggested that discrepancies in the data themselves, especially at higher temperatures, may be the reason for this. It is the opposite for

the excess molar volume model. The model was very consistent for different data sets and for a wider range of temperatures (see Fig. 1a). We thus suggest that the excess Henry's constant can be correlated with the excess molar volume according to Eq. 8. A comparison for predicted excess Henry's constants can be seen in Fig. 2.

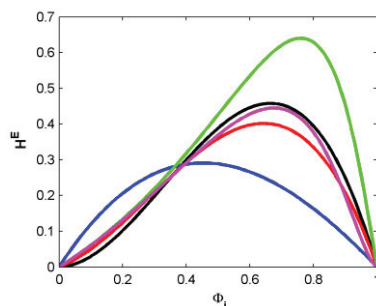


Figure 2. Model predictions for the Excess Henry's constant at 30°C (—, [8]; —, [12]; —, [13]; —, [3]; —; this work).

The Henry's constant is then calculated from the excess Henry's constant according to Eq. 6 and the inconsistencies of the three models blow up as can be seen in Fig. 3a. The first model [8] was regressed to data up to 40°C, thus it would be expected only to be valid up to this temperature and fail at higher temperature. The second model [12] used data at higher concentrations of MEA (6M) and for three temperatures (30, 35 and 40°C). The suggested parameters from this model represent the data well for different temperatures, but shows discrepancies of more than 5% at some concentrations (see Fig. 3b). The third model [13] was developed based on own data only and the model does not work properly at higher temperatures.

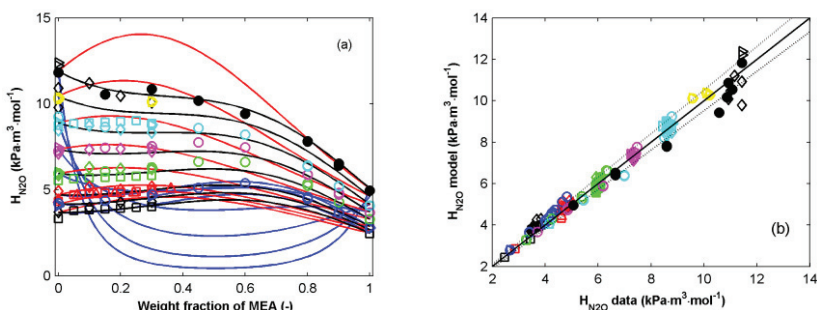


Figure 3. The Wang's model for (a) the N₂O solubility in the MEA/H₂O system as a function of temperature and concentration (—, [8]; —, [12]; —, [13]); (b) Parity plot with the best suggested parameters [12] (solid line, diagonal; dashed lines, ±5%).

In the present model only N₂O solubility into water and pure MEA are necessary. These are presented in Fig. 4 for different sets of data. Fig. 4a shows that the N₂O solubility data into water agree quite well up to 80°C while at higher temperatures discrepancies appear. Five different correlations have been suggested and can be classified into 2 groups. The first group [5,14] shows that the solubility rapidly increases with increasing temperature. This can be understood based on the lack of supporting data at higher temperatures. The second group [3,4,7] provide different correlations but which give a similar trends up to higher temperatures

(up to 120°C). It is also seen that our own data [3] agree very well with the data collected at higher pressures with a different technique [7].

Data for N₂O solubility into pure MEA were collected from different sources and it is seen in Fig. 4b that the data are scarcer than for water but the discrepancies are still acceptable and within ±5%. We propose two correlations for the N₂O solubility into water and MEA as:

$$\ln H_{N_2O-H_2O} = -700.6501 + 14905.5017/T + 126.3505 \cdot \ln T - 0.2276 \cdot T \quad (11)$$

$$\ln H_{N_2O-MEA} = 3.9451 - 589.9365/(T - 99.0406) \quad (12)$$

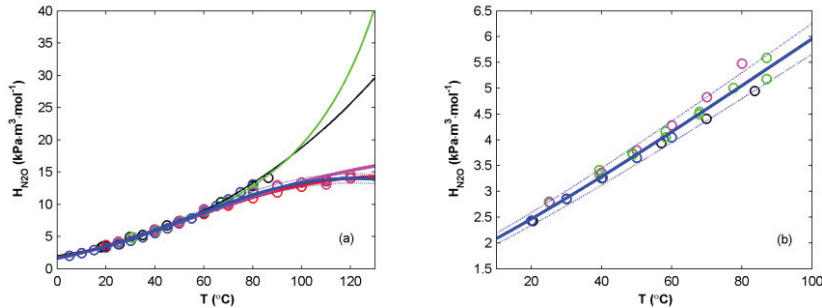


Figure 4. Prediction of N₂O solubility in (a) H₂O (○, [2]; ○, [3]; ○, [4]; ○, [5]; ○, [13]; —, [5]; —, [14]; —, [4]; —, [7]; —, This work, ---, ±5%). (b) Pure MEA as a function of temperature (○, [2]; ○, [3]; ○, [8]; ○, [13]; solid line, this work; dashed lines, ±5%).

By substituting Eq. 10, 11 and 12 into Eq. 9, the model of this work can be plotted with the data in Fig. 5a. The model can represent very well the data set from 20-80°C, however it is observed that at 80°C some points have more than ±5% deviation. As was mentioned previously, the proposed parameters from [12] gave the best representation of Wang's model for N₂O solubility into aqueous MEA solution. However, it should be noted that the Wang model requires not only N₂O solubility into water and pure alkanolamine but it also needs measurements from aqueous solutions at different concentrations and temperatures.

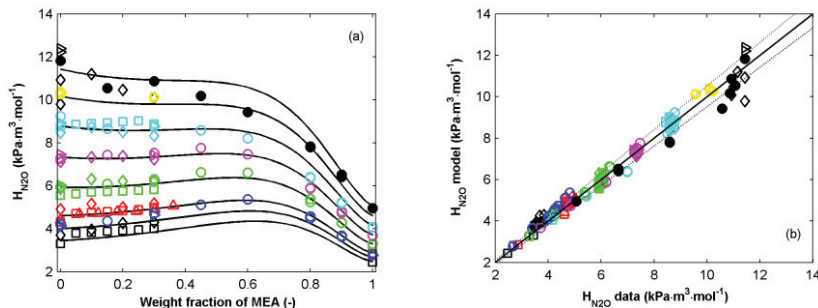


Figure 5. Model predictions for (a) N₂O solubility in the MEA/H₂O system as a function of temperature and concentration (solid lines, model; ▷, [2]; ○/●, [3]; ◇, [7]; □, [13]; △, [15]), (b) the parity plot (solid line, diagonal; dashed lines, ±5%).

4. Conclusion

A N₂O solubility model was developed based on excess volume to estimate the excess Henry's constant. It only requires density data for the solvent mixtures and N₂O solubility into the two solvents, in this case water and pure alkanolamine. Data of N₂O solubility into water and MEA were collected and correlated. The suggested correlations gave an uncertainty within $\pm 5\%$. The new simplified N₂O solubility model works well and represent the data within an uncertainty of $\pm 5\%$ up to 80°C. However, at higher temperatures, some points have more than 5% deviation.

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