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Comparative Study of Electrolyte Thermodynamic Models for Carbon Dioxide Solubility in Water at High Pressure

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The electrolyte thermodynamic models have been extensively studied for carbon dioxide – water system for the prediction of vapour liquid equilibrium at low pressures. However, no guidelines are available for selection of electrolytic models which are applicable at high pressure for prediction of thermodynamic properties. In this study, solubility prediction of limited Debye Huckel (DH), Pitzer Debye Huckel (PDH) and modified Three Characteristic Parameter Correlation (mTCPC) electrolyte models have been tested for a wide range of temperature (273 – 453 K) and pressure (0.1 – 7.2 MPa).The comparative study shows that introduction of electrolyte model improves the prediction accuracy when physical solubility of gas is low, either in high temperature or low pressure region. The mTCPC model gives improved prediction than non-electrolyte model but requires additional parameters and complex calculations. New values for binary interaction parameters of UNIFAC for carbon dioxide – water system are also optimized.

1. Introduction

Absorption of carbon dioxide in water has found extensive applications in chemical process industries such as beverages, enhanced oil recovery, carboxylic acids, etc. Moreover, the recent developments in carbon capture have focused on solubility of carbon dioxide in water based solvents. The knowledge of vapour-liquid equilibrium (VLE) of the CO_2 – H_2O system is a key factor in the design of such chemical processes (Kohl, 1997) and associated process development, like oil and gas sector (Nguyen et al., 2014). Since CO_2 slightly dissociates into ionic species upon dissolution in water, a lot of research has been channelled to discuss the effect of ionic equilibria at low pressures and temperatures (Edwards et al., 1978), but has limited information at high pressures. Chapoy et al. (2004) applied equation of state / excess Gibbs energy model (EoS/G^E) to predict VLE for CO_2 – H_2O system for medium pressure range and low temperatures. Valtz et al. (2004) compared semi-empirical, EoS/G^E and statistical thermodynamic modelling techniques for limited pressure and temperature. Both studies neglected the ionic equilibria in liquid phase. The importance of ionic equilibria in modelling has been detailed by Li Yuen Fong et al. (2014).

The purpose of this study is to analyze the effect of electrolytic correction on prediction of carbon dioxide solubility in water. The study encompasses a large data with range of pressures (0.1 – 7.2 MPa) and temperatures (273 – 453 K).

2. Experimental Data

The experimental data was taken from published literature and is given in Table 1.

3. Determination of Liquid Phase Ionic Equilibria

The dissociation of carbon dioxide in water is represented by following reactions (Edwards et al., 1978), where k_1, k_2 and k_3 represents the equilibrium constants for reactions given in Eq(1) to Eq(3).

$$CO_2 + H_2O \overset{k_1}{\rightleftharpoons} HCO_3^- + H^+ \Rightarrow [HCO_3^-] = \frac{k_1[CO_2]}{[H^+]} \tag{1}$$

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$$HCO_3^- \overset{k_2}{\rightleftharpoons} CO_3^{-2} + H^+ \Rightarrow [CO_3^{-2}] = \frac{k_2[HCO_3^-]}{[H^+]} = \frac{k_1k_2[CO_2]}{[H^+]^2} \qquad (2)$$

$$H_2O \overset{k_3}{\rightleftharpoons} OH^- + H^+ \Rightarrow [OH^-] = \frac{k_3}{[H^+]} \qquad (3)$$

Table 1: Sources of Experimental Data for Carbon Dioxide – Water VLE Equilibrium

Data Source	No. of Data Points	Temperature (K)	Pressure (MPa)
Bamberger et al.(2000)	12	323 – 353	4.05 – 7.08
Campos et al. (2009)	17	303 – 323	0.10 – 0.54
Dalmolin et al. (2006)	33	288 – 308	0.11 - 0.47
Han et al.(2011)	16	313 – 333	0.37 – 2.00
Houghton et al. (1957)	103	273 – 373	0.10 – 3.65
Lucile et al. (2012)	29	298 – 373	0.54 – 5.14
Muller et al.(1988)	48	373 – 453	0.60 – 7.21
Stewart and Munjal (1970)	10	273 – 285	1.01 – 4.56
Valtz et al. (2004)	32	298 – 318	0.51 -7.03
Zawisza and Malesinska (1981)	27	323 – 453	0.15 – 4.62

The electro-neutrality equation of the dissociation is given as follows

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{-2}] \qquad (4)$$

Substituting values of ionic species and solving Eq(4) for hydrogen ion $[H^+]$

$$[H^+]^3 + (k_1[CO_2] + k_3)[H^+] + 2k_1k_2[CO_2] = 0 \qquad (5)$$

The concentration of carbon dioxide in liquid, $[CO_2]$ is determined by Henry's law relationship.

$$P_{CO2} = H_{CO2}[CO_2] \qquad (6)$$

The values of equilibrium constants for formation of bicarbonate (k_1), carbonate (k_2), hydroxyl (k_3) ions and Henry's constant (H_{CO2}) are taken from Edwards et al. (1978). The concentration of hydrogen ion is calculated from roots of the equation and value of $[H^+]$ was selected between range of 10^{-3} and 10^{-7} (corresponding to the pH value of 3 and 7 for carbonic acid). Subsequent values of carbonate, bicarbonate and hydroxyl ions are found using corresponding equilibrium constants.

4. Thermodynamic Model

4.1 Base Model – (translated modified Peng-Robinson – LCVM – UNIFAC)

Linear Combination of Vidal and Michelsen mixing rule (Boukouvalas et al., 1994) has been used to correlate excess Gibbs energy function with Translated Modified Peng Robinson equation of state (Magoulas and Tassios, 1990). The excess Gibbs energy function (G^E) consists of two forces, namely short range and long rang forces and given by

$$G^E = G^E_{UNIFAC} + G^E_{ELECTROLYTE(DH,PDH \text{ or } mTCPC)} \qquad (7)$$

The short range forces are determined by Universal Functional Activity Coefficient (UNIFAC) local composition model (Fredenslund et al., 1975). The long range forces are calculated by Limited Debye Huckel (Debye and Hückel, 1923), Pitzer Debye Huckel (Pitzer, 1973) or Modified Three Character Parameter Correlation electrolyte equations (Ge et al., 2007) in three different models, discussed further in following sections.

4.2 Model 1 – Limited Debye Huckel Law with tmPR – LCVM – UNIFAC

The limited Debye Huckel law is a reduced form of Debye Huckel equation that is applicable for weak solutions (0.01 molal).

$$G^E_{\text{Limited Debye Huckel}} = \sum_{i=1}^{i} x_i \left(-Az_i^2\sqrt{I}\right) \qquad (8)$$

where A is the Debye Huckel constant, z is the charge on specie and I is the ionic strength of solution. Subscript i represents ionic specie in liquid phase.

4.3 Model 2 – Pitzer Debye Huckel with tmPR – LCVM – UNIFAC

The Pitzer Debye Huckel equation for electrolytes was developed by Pitzer. The model is applicable up to molalities of 6.0 with good prediction and given by Eq(9). Constants *B* and *C* are second and third virial coefficients and are fitted to experimental data. Constant *b* represents the ionic radius of the ions in the system.

$$G^E_{\text{Pitzer Debye Huckel}} = \sum_{i=1}^{i} x_i \left(-z_i^2 A \left[\frac{I^{0.5}}{1+bI^{0.5}} + \frac{2}{b}\ln(1+bI^{0.5}) \right] + m_i v_i B + 2m_i^2 v_i^{1.5} C \right) \tag{9}$$

where *m* and *v* are molality and stoichiometric coefficients of species.

4.4 Model 3 – Modified Three Characteristic Parameter Correlation with tmPR – LCVM – UNIFAC

The mTCPC model is applicable up to 6.0 molal. Constants b, S and n are fitting parameters, whereas T represents temperature.

$$G^E_{\text{mTCPC}} = \sum_{i=1}^{i} x_i \left(-z_i^2 A \left[\frac{I^{0.5}}{1+bI^{0.5}} + \frac{2}{b}\ln(1+bI^{0.5}) \right] + \frac{S}{T}\frac{I^{2n}}{v_i} \right) \tag{10}$$

4.5 Determination of Interaction and Fitting Parameters

The binary energy interaction parameters (BIP) for UNIFAC and fitting parameters for mTCPC were optimized by following objective function.

$$OF = \frac{1}{N}\sum_{i=1}^{N} \left(\frac{\left| x_{\text{calc}} - x_{\text{exp}} \right|}{x_{\text{exp}}} \right) \tag{11}$$

where x_{calc} and x_{exp} are the calculated and experimental solubility of carbon dioxide. The optimized values are given in Table 4 and compared to published literature for base model only.

Table 2: Binary Interaction Parameters for UNIFAC

Model	Binary Interaction Parameters *				Electrolytic Interaction Parameters **		
	a_{12}	a_{21}	b_{12}	b_{21}			
Base Model	610.49	283.12	-2.93	2.72			
Literature (Voutsas et al., 1996)	601.10	271.80	-2.91	2.75			
Model 1 (LDH)	636.22	289.92	-2.64	2.89			
Model 2 (PDH)	636.22	289.92	-2.64	2.89	0.00 (*b*)	0.00 (*B*)	0.00 (*C*)
Model 3 (mTCPC)	634.46	287.83	-2.67	2.99	1.18 (*b*)	0.98 (*S*)	0.64 (*n*)

** Subscript 1 and 2 represents carbon dioxide and water.*
***The constants for electrolytic interaction parameters for electrolyte equation have been given in brackets.*

The fitting parameters for PDH were found insensitive (0.013 %) to solubility data of carbon dioxide in water. Hence, the original Debye Huckel equation was maintained for calculation due to low ionic strength, which veritably explains similar values of BIP in model 1 and 2. On the other hand, the values of fitting parameters (*b*, *S* and *n*) for mTCPC-LCVM model were maintained due to considerable effect on solubility prediction (16.75 %). Moreover, the solvation term in mTCPC-LCVM model explains the formation of ionic equilibria in liquid phase (Solbraa, 2002).

5. Results and Discussion

Table 3 compares the prediction of optimized UNIFAC BIP (in this study) with literature. Prediction of carbon dioxide solubility has been improved by newly optimized UNIFAC BIP values without an effect on vapor phase prediction, as compared to the prediction by BIP values found in literature. The root mean square error (RMSE) and mean absolute error (MAE) has reduced substantially in liquid phase prediction.
Figure 1 compares the VLE prediction of LCVM (base) model at various temperatures and pressures with newly optimized BIP and BIP available in literature. The prediction of carbon dioxide solubility in water has been improved by newly optimized UNIFAC BIP in this study.

Table 3: Comparison of performance of BIP taken from literature and BIP optimized in this study

Model Type	Liquid Phase			Vapour Phase		
	No. of Data Points	RMSE ($x10^{-4}$)	MAE ($x10^{-4}$)	No. of Data Points	RMSE ($x10^{-2}$)	MAE ($x10^{-2}$)
Base Model	313	7.84	4.96	105	4.79	2.91
Literature (Voutsas et al., 1996)	313	11.25	5.73	105	4.92	2.94

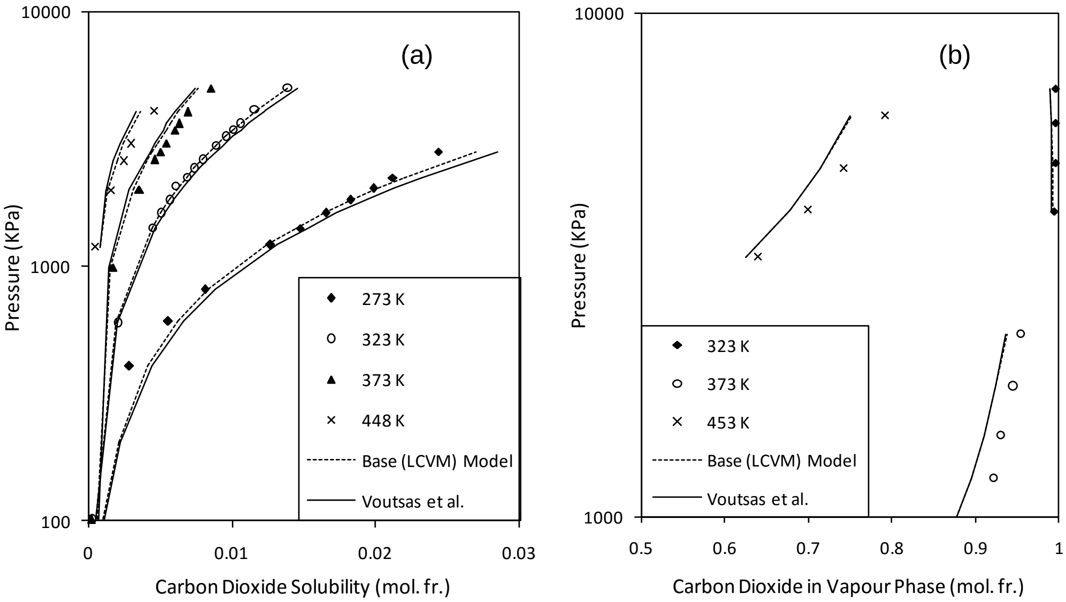

Figure 1: Comparison of VLE prediction of BIP found in literature (Voutsas et al., 1996) and optimized (in this study) against experimental data at various temperatures for liquid (a) and vapour (b) phase

Table 4 compares RMSE and MAE for liquid phase prediction among electrolytic models. Figure 2 represents the parity graphs for liquid phase prediction for base model, model 1, model 2 and model 3.

Table 4: Comparison of Electrolytic Models for Carbon Dioxide – Water System

Model Type	No. of Points	RMSE ($x10^{-4}$)	MAE in liquid phase ($x10^{-4}$)
Base Model	313	7.84	4.96
Model 1		7.36	5.20
Model 2		7.36	5.20
Model 3		7.15	4.89

The performance of all four models is comparable. The mTCPC – LCVM model has the smallest error but has trade-offs to introduce three new fitting parameters and complex calculations. Contrarily, base model efficiently predicts the discussed system without using complex set of equations, with slight loss of accuracy as compared to mTCPC – LCVM model.

6. Conclusions

At high pressures, introduction of primitive electrolytic models (DH and PDH) have a negative effect over the accuracy of prediction, while the mTCPC – LCVM model improves prediction accuracy, slightly, but involves complex calculations. Therefore, the selection between base model and mTCPC – LCVM model has certain trade-offs. In case, the ionic strength is increased (like carbon dioxide absorption in saline water or aqueous alkanolamine solutions), the mTCPC – LCVM model will positively outperform base model.

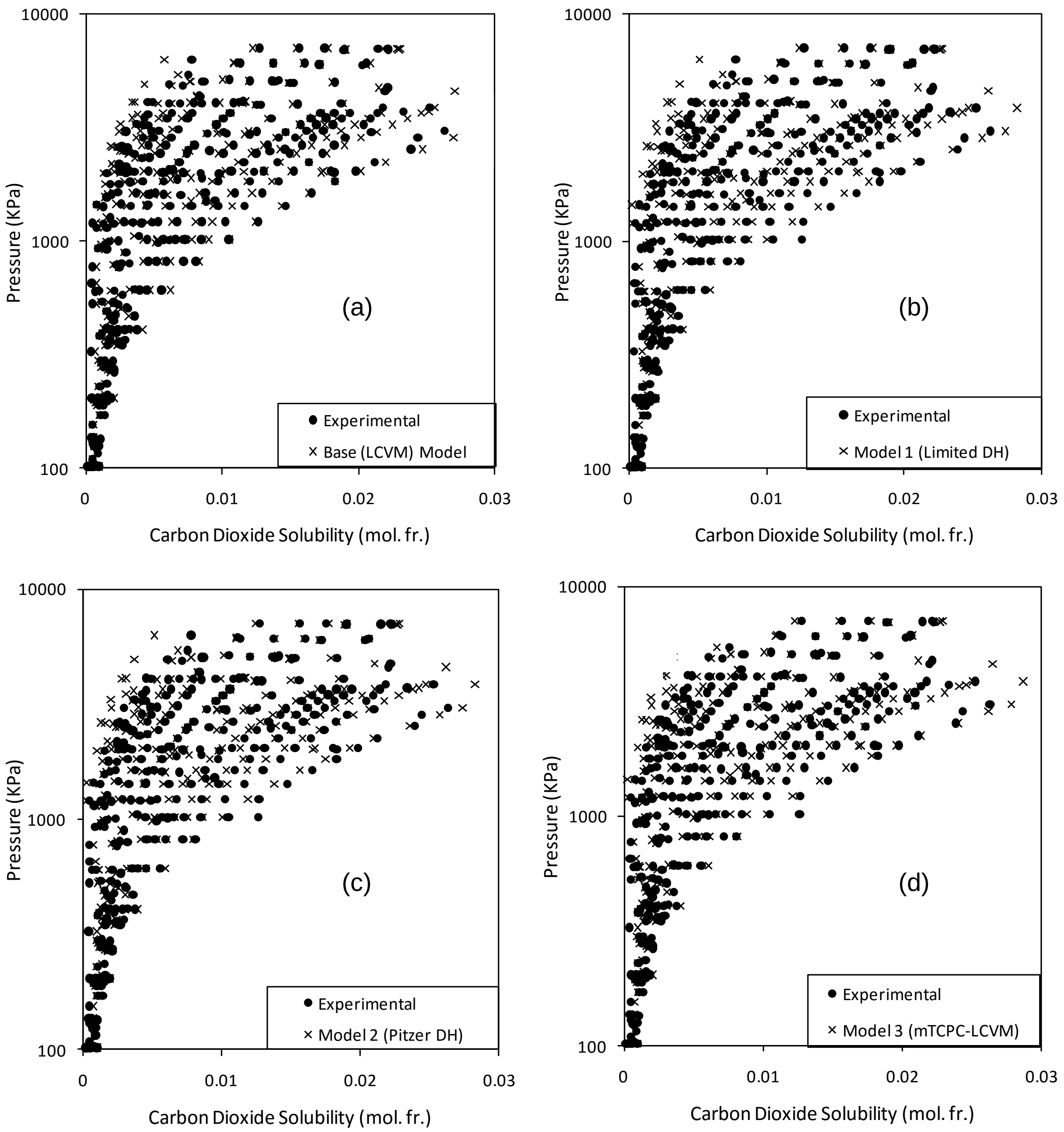

Figure 2: Comparison of prediction by base model (a), model 1 (b), model 2 (c) and model 3 (d) against experimental values

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