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# A consistent thermodynamic model for Solid Liquid Equilibrium (SLE) and Vapor Liquid Equilibrium (VLE) in aqueous amine solutions

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## Abstract

Two thermodynamic models (NRTL/UNIQUAC) were tested to model the SLE and VLE of the aqueous piperazine system. The reported 6 species in solid and liquid phases were represented successfully together with the estimated standard enthalpies and Gibbs energy of formation. The earlier reported experimental data for different SLE and VLE were found to be very useful for this work. The models consistently represent the experimental data. However, efforts are still needed to improve the model and a direct measurement of the solution heat capacity will reduce the number of fitted parameters.

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## 1. Introduction

Reliable and consistent SLE and VLE data are required to develop rigorous thermodynamic models. Such models based on excess Gibbs energy (NRTL [1] and UNIQUAC [2]) have advantages by being able to represent both Solid-Liquid-Equilibrium (SLE) and Vapor-liquid-Equilibrium (VLE) in aqueous amine systems [3], carbonate

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systems [4] and amine/ carbonate systems [5,6]. Robust and accurate modeling relies on the quality and type of data used to regress the model parameters, and on a robust fitting procedure to obtain the best representation of the data.

SLE data could cover the equilibria with ice, with possible hydrates and with complex salt forming systems such as in the piperazine water system. In this system, at a specific temperature and concentration, different equilibrium can occur according to [7]:

Vapor Liquid Equilibria (VLE)



Solid Liquid Equilibria (SLE)



Water and piperazine molecules exist in the vapor, liquid and solid phases while formation of solid piperazine-hexahydrate ( $Pz \cdot 6H_2O_{(s)}$ ) and piperazine-hemihydrate ( $Pz \cdot 0.5H_2O_{(s)}$ ) occur at higher Pz concentration.

To represent the two types of equilibrium (VLE and SLE), a minimization of excess Gibb's energy can be used to describe speciation at chemical equilibrium. The equilibrium constant of each reaction is temperature dependent and commonly represented by four parameters as:

$$\ln K_i = A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T \quad (7)$$

Another method, based on the Gibbs-Helmholtz equation, can be used to derive the equilibrium constants according to [3-6]

$$\frac{d \ln K_{T,P_o,k}}{dT} = \frac{\Delta_k H_{T,P_o}^\circ}{R \cdot T^2} \quad (8)$$

$$\frac{d \Delta_k H_{T,P_o}^\circ}{dT} = \Delta_k C_p^\circ(T, P_o) \quad (9)$$

Where  $\Delta_k$  is the difference between products and reactants in a reaction.

If the heat capacity can be correlated as:

$$\Delta_k C_{p,i}^\circ = \Delta a_i + \Delta b_i \cdot T + \frac{\Delta c_i}{T - T_\theta} \quad (10)$$

Then the change in enthalpy ( $\Delta_k H_{T,P_o}^\circ$ ) can be written as:

$$\Delta_k H_{T,P_o}^\circ = \Delta_k H_{T_o,P_o}^\circ + \Delta a_i \cdot (T - T_o) + 0.5 \cdot \Delta b_i \cdot (T^2 - T_o^2) + \Delta c_i \cdot \ln \left( \frac{T - T_\theta}{T_o - T_\theta} \right) \quad (11)$$

Finally, expressions for the equilibrium constants ( $K_{T,P_o,k}$ ) at different temperatures for reactions 3-6 can be obtained via integration of equation 7 giving:

$$R \cdot \ln K_{T,P_o,k} = -\frac{\Delta_k G_{T_o,P_o}^\circ}{T_o} - \Delta_k H_{T_o,P_o}^\circ \left( \frac{1}{T} - \frac{1}{T_o} \right) + \Delta a_i \cdot \left( \ln \frac{T}{T_o} + \frac{T_o}{T} - 1 \right) + 0.5 \cdot \Delta b_i \cdot \left( \frac{(T-T_o)^2}{T} \right) + \frac{\Delta c_i}{T_o} \cdot \left( \frac{T-T_o}{T} \cdot \ln \frac{(T-T_o)}{(T_o-T_o)} - \ln \frac{T}{T_o} \right) \quad (12)$$

Where  $K_{T,P_o,k} = \prod_k a_k^{v_k} = \prod_k (\gamma_k \cdot x_k)^{v_k}$

The infinite dilution reference state was used for piperazine  $Pz_{(l)}$  while for the solid phase, pure solid was used as reference state. Values for standard state chemical potentials can be found in the literature for solids, liquids and gases at 298.15K and 1 bar, such as reported in the NSB database [8] as well as in the NIST-JANAF thermodynamic tables [9].

Equation 12 shows that the composition of the solution can be calculated at a certain temperature if activity coefficients are known for water and piperazine at this temperature from any selected thermodynamic model (NRTL [1], UNIQUAC [2]). The activity coefficients for water and piperazine can be determined through the gamma-phi method from VLE data and such data can be produced from an ebulliometer study [10, 11]. SLE data are usually gathered from freezing point depression measurements [7]. This indicates that one set of parameters for the selected thermodynamic model, for water and piperazine, can be implemented to represent the species in all phases.

Some of the standard thermodynamic properties at 298.15 K and 1 bar ( $\Delta_k G_{T_o,P_o}^\circ, \Delta_k H_{T_o,P_o}^\circ, \Delta_k C_{p,i}^\circ$ ) were collected from the literature. If reported data were unavailable, these values were estimated in the fitting procedure, i.e. used as fitted parameters.

## 2. Modeling Part

To obtain the thermodynamic parameters in the selected model, the collected data from the literature were fitted using an in-house Matlab code for multi-response parameters estimation (Modfit) [12] with the objective function (OF) being the sum of relative square error of each response (total pressure, activity coefficient, excess heat and freezing point depression).

$$OF = \min \sum_i^n \left| \frac{y_i^{Exp.} - y_i^{Calc.}}{y_i^{Exp.}} \right| \quad (13)$$

$$\text{with an AARD (\%)} = \frac{100}{n} \sum_i^n \left| \frac{y_i^{Exp.} - y_i^{Calc.}}{y_i^{Exp.}} \right|$$

The experimental responses ( $y_i^{Exp.}$ ) were obtained from the reported VLE results [10, 11] and the SLE results [7] respectively.

## 3. Results and discussion

Fosbøl et al [5] have previously done a similar work in the Piperazine and water system. They demonstrated the ability of the e-UNIQUAC model in representing a complex system such  $Pz \cdot KOH \cdot K_2CO_3 \cdot KHCO_3 \cdot H_2O$ . However no thermo-physical properties were reported to compare with the results. The collected thermo-physical data used in this work are shown in Table 1. The standard enthalpy and Gibbs energy of formation of  $Pz \cdot 6H_2O_{(s)}$  and  $Pz \cdot 0.5H_2O_{(s)}$  were estimated in the present work from the NRTL and UNIQUAC models. This was also done for the standard Gibbs energy of formation of  $Pz_{(l)}$ . The heat capacities for the solids were estimated from a correlation based on a modified Kopp's Rule [15]. The NRTL and UNIQUAC models predicted very similar values for the

standard enthalpy and Gibbs energy of formation for  $Pz \cdot 6H_2O_{(s)}$ , but a significant difference was seen for the standard enthalpy of  $Pz \cdot 0.5H_2O_{(s)}$ .

Table 1. Thermo physical properties of the system

No.	Species	Phase	$\Delta_k G_{T_o, P_o}^\circ$ ( $\frac{kJ}{mol}$ )	$\Delta_k H_{T_o, P_o}^\circ$ ( $\frac{kJ}{mol}$ )	$\Delta_k C_p^\circ(T, P_o)$ ( $J/mol \cdot K$ )			Source(s)
					$\frac{a}{(\frac{J}{mol \cdot K})}$	$\frac{b}{(\frac{J}{mol \cdot K^2})}$	$\frac{c}{(\frac{J}{mol})}$	
1	$H_2O$	$\ell$	-237.129	-285.830	58.37	0.039	523.88	[4]
		$s$	-236.538	-292.624	47.90	0	0	[4]
2	$Pz$	$\ell$	$\frac{239.972\#}{239.583^*}$	-18.500	42.47	0.542	0	[13]
		$s$	240.200	-40.970	-46.90	0.472	0	[13,14]
3	$Pz \cdot 6H_2O$	$s$	$\frac{-1190.618\#}{-1191.285^*}$	$\frac{-1775.723\#}{-1775.140^*}$	327.88	0	0	[15]
			121.531#	-176.726#	170.91	0	0	[15]
4	$Pz \cdot 0.5H_2O$	$s$	$\frac{120.467^*}{120.467^*}$	$\frac{-184.963^*}{-184.963^*}$	170.91	0	0	[15]

#Estimated with the NRTL model from the  $\Delta_k G_{T_o, P_o}^\circ$  and  $\Delta_k H_{T_o, P_o}^\circ$  of the selected reaction.

\*Estimated with the UNIQUAC model from the  $\Delta_k G_{T_o, P_o}^\circ$  and  $\Delta_k H_{T_o, P_o}^\circ$  of the selected reaction.

The new thermodynamic parameters for both models are shown in Table 2. Efforts was made to keep the previous reported parameters [10] in the optimization routine, but this was not successful. The new reported values here are slightly different compared to the previous work [10] since new SLE data were included. It might also be an indication that the earlier reported parameters did not find a global optimum value.

Table 2. NRTL and UNIQUAC Binary interaction parameters

NRTL			
$a_{Pz-H_2O}$	$-2.51 \pm 0.9$	$a_{H_2O-Pz}$	$11.76 \pm 2$
$b_{Pz-H_2O}$	$231.17 \pm 357$	$b_{H_2O-Pz}$	$-4159.87 \pm 710$
UNIQUAC			
$u_{Pz-H_2O}^\circ$	$-483.49 \pm 30$	$u_{H_2O-Pz}^\circ$	$-167.38 \pm 19$
$u_{Pz-H_2O}^T$	$-5.13 \pm 0.6$	$u_{H_2O-Pz}^T$	$-2.07 \pm 0.3$

The representation produced by the two thermodynamic models for VLE and SLE can be seen in figures 1 and 2. The two models were able to predict well the VLE data in figure 1 and the SLE data in figure 2. However it seen in figure 2 that both models under-predict the melting point of pure piperazine.

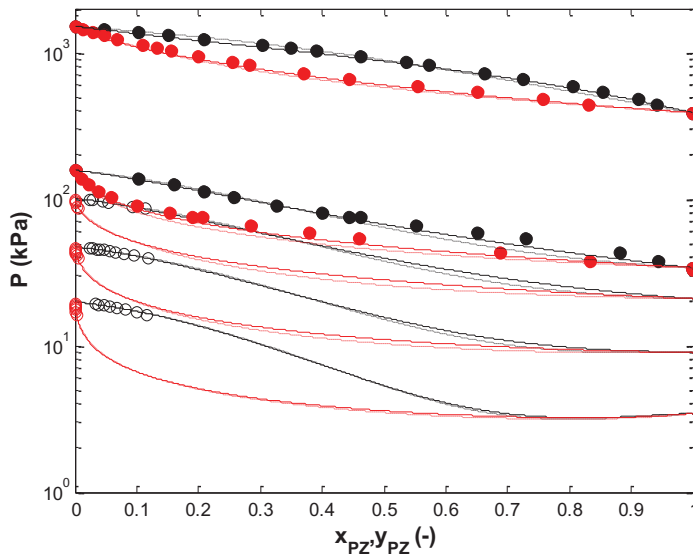


Figure 1. Vapor Liquid Equilibrium of Pz + H<sub>2</sub>O system at different temperatures (Filled Points, [11]; Unfilled Points, [10]; Dash line, NRTL; Solid line, UNIQUAC)

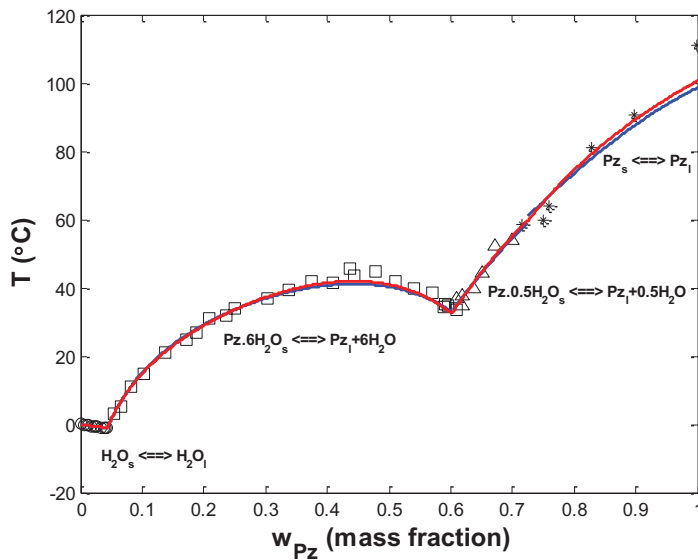


Figure 2. Solid Liquid Equilibrium of Pz + H<sub>2</sub>O system at different temperatures (data, [7]; Blue solid line, NRTL; Red solid line, UNIQUAC)

The goodness of both models is also presented by the AARD values in Table 3. It is seen that the models work successfully. They give a similar trend in AARD values, but the UNIQUAC model seems slightly better than the NRTL due to one extra parameter. The AARD values in this work are also improved compared to previous reported work [10].

Table 3. Absolute average relative deviation (AARD) of NRTL and UNIQUAC models

No.	Experiment Type	Reactions Number	Variables Type	Number of data (N)	AARD (%)	
					NRTL	UNIQUAC
1	VLE	1 and 2	$\gamma_{Pz}$	24	8.4	8.4
			$P_T$	34	4.5	3.1
2	SLE	3	$\theta_3^F$	12	9.0	9.0
		4	$\theta_4^F$	24	5.6	4.7
		5	$\theta_5^F$	7	5.3	3.5
		6	$\theta_6^F$	6	9.8	7.0
3		Total		107	6.5	5.5

#### 4. Conclusion

Two thermodynamic models (NRTL/UNIQUAC) were tested to model the SLE and VLE of the aqueous piperazine system. The reported 6 species in solid and liquid phases were represented successfully together with the estimated standard enthalpies and Gibbs energy of formation. The earlier reported experimental data for different SLE and VLE were found to be very useful for this work. The models consistently represent the experimental data. However, efforts are still needed to improve the model and a direct measurement of the solution heat capacity will reduce the number of fitted parameters.

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