

# CORRELATION OF SOLUBILITIES FOR CO<sub>2</sub> AND NH<sub>3</sub> IN H<sub>2</sub>O USING SOAVE - REDLICH - KWONG EQUATION OF STATE WITH MHV2 MIXING RULE

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The flexibility and applicability of the modified Huron-Vidal second order (MHV2) mixing rule have been examined for the correlation of solubilities for CO<sub>2</sub> and NH<sub>3</sub> in H<sub>2</sub>O as an example of a system containing volatile weak electrolytes. The MHV2 mixing rule is one of the excess Gibbs energy ( $g^E$ ) mixing rules. The  $g^E$  mixing rules are well known to be able to predict vapor-liquid equilibria (VLE) of polar or non-polar mixture systems under high pressure. We have used the Soave-Redlich-Kwong equation of state (SRK-EOS) with the MHV2 mixing rule. Assuming a series reaction between CO<sub>2</sub> and NH<sub>3</sub> in the aqueous phase and the temperature dependence of the equilibrium constant, the solubility behavior of the CO<sub>2</sub>-NH<sub>3</sub>-H<sub>2</sub>O system can be correlated with reasonable accuracy.

## Introduction

Recently, many studies for correlation of vapor-liquid equilibria (VLE) of a system containing volatile weak electrolyte, such as a CO<sub>2</sub>-NH<sub>3</sub>-H<sub>2</sub>O system, have been reported<sup>2, 6, 7, 8</sup>. They have used solution models or various equations of state with the mixing rule. In our previous paper<sup>16</sup>, we applied the perturbed hard-sphere equation of state (PHS-EOS) with the mixing rule based on the local mole fraction concept (LMFC) to correlation of VLE of the CO<sub>2</sub>-NH<sub>3</sub>-H<sub>2</sub>O system under conditions for the urea synthesis process. In that application, the interaction parameters  $k_{ij}$  and  $\alpha_{ij}$  in the LMFC mixing rule were used as the fitting parameters and its application was restricted.

On the other hand, the good applicability of the excess Gibbs energy ( $g^E$ ) mixing rule to the prediction of binary and multi-component VLE compositions over a wide range of temperatures and pressures was pointed out<sup>15</sup>. Furthermore, the ability of the modified Huron-Vidal second order (MHV2) mixing rule, which is one of the  $g^E$  mixing rules, for predictions of high pressure VLE<sup>5</sup> and VLE of the system containing strong electrolyte<sup>15</sup> has been also shown. However, the applicability of the  $g^E$  mixing rule for prediction of VLE of the system containing volatile weak electrolyte has been rowely reported.

In this paper, we examined the flexibility of the Soave-Redlich-Kwong equation of state (SRK-EOS) with the MHV2 mixing rule for correlation of solubilities for CO<sub>2</sub> and NH<sub>3</sub> in H<sub>2</sub>O under high pressure.

## 1. Thermodynamic Model

### 1.1 Equation of state

Following Dahl *et al.*<sup>3, 4</sup>, we adopt the SRK-EOS<sup>21</sup>.

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (1)$$

where  $a$  and  $b$  are the EOS parameters and the pure component parameters  $a_{i,i}$  and  $b_{i,i}$  are given using the corresponding state<sup>14, 21</sup>.

$$a_{i,i} = 0.4286 \frac{R^2 T_{c,i}^2}{P_{c,i}} f(T_{r,i})^2 \quad (2)$$

$$b_{i,i} = 0.08664 \frac{RT_{c,i}}{P_{c,i}} \quad (3)$$

with

$$f(T_{r,i}) = \begin{cases} 1 + C_1(1 - T_{r,i}^{0.5}) + C_2(1 - T_{r,i}^{0.5})^2 \\ \quad + C_3(1 - T_{r,i}^{0.5})^3 & (T_{r,i} < 1) \\ 1 + C_1(1 - T_{r,i}^{0.5}) & (T_{r,i} > 1) \end{cases} \quad (4)$$

where constants  $C_1$ ,  $C_2$  and  $C_3$  are determined from the vapor pressures of the pure components. Values of the critical properties and constants for pure components are determined in this work and shown in **Table 1**.

### 1.2 Mixing rule

The MHV2 mixing rule<sup>3, 4, 5, 10, 15</sup> for the mixture parameters is given as follows.

$$\begin{aligned} q_1 \left( \alpha_{\text{mix}} - \sum_i x_i \alpha_{i,i} \right) + q_2 \left( \alpha_{\text{mix}}^2 - \sum_i x_i \alpha_{i,i}^2 \right) \\ = \frac{g_0^E}{RT} + \sum_i x_i \ln \left( \frac{b_{i,i}}{b} \right) \end{aligned} \quad (5)$$

where  $\alpha_{\text{mix}} = a/bRT$ ,  $\alpha_{i,i} = a_{i,i}/b_{i,i}RT$  and  $b = \sum_i x_i b_{i,i}$ . The recommended values of  $q_1$  and  $q_2$  are -0.478 and -0.0047,

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**Table 1** Critical properties and constants for pure substance<sup>14, 19)</sup>

Substance	$T_c$ [K]	$p_c$ [MPa]	$C_1$ [-]	$C_2$ [-]	$C_3$ [-]
CO <sub>2</sub>	304.2	7.38	0.8653	-0.4386	1.3447
NH <sub>3</sub>	405.6	11.28	0.8625	0.0000	0.0000
H <sub>2</sub> O	647.3	22.05	1.0873	-0.6377	0.6345

**Table 2** Molecular  $R_k$  and  $(z/2) Q_k$  and the main group definitions<sup>3, 15)</sup>

Main Group	Subgroup	$R_k$	$(z/2) Q_k$
CO <sub>2</sub>	CO <sub>2</sub>	2.5920	2.522
NH <sub>3</sub>	NH <sub>3</sub>	0.6948	1.150
H <sub>2</sub> O	H <sub>2</sub> O	0.9200	1.400

**Table 3** Modified UNIFAC interaction parameters  $a_{ij, k}$  ( $k = 1$  or 2)

$i$	$k$	$j$		
		CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O
CO <sub>2</sub>	1	0.0	48.48	1360.0
	2	0.0	2.955	0.0
NH <sub>3</sub>	1	-123.8	0.0	-272.7
	2	-0.6	0.0	0.5122
H <sub>2</sub> O	1	197.0	-149.6	0.0
	2	0.0	0.3121	0.0

respectively<sup>5)</sup>. Since all the parameters are known in Eqs. (1)-(4) and  $g_0^E$  can be calculated from the  $g^E$  model (here modified UNIFAC), we can solve Eq. (5) for  $\alpha_{\text{mix}}$  yielding the mixture parameters for the EOS.

The fugacity coefficient is given by

$$\ln \phi_i = \ln \left[ \frac{RT}{p(v-b)} \right] + \left( \frac{1}{v-b} - \frac{\alpha}{v+b} \right) b_{i,i} - \ln \left( \frac{v+b}{v} \right) \left\{ \frac{\partial (n\alpha)}{\partial (n_i)} \right\} T, n_j \quad (6)$$

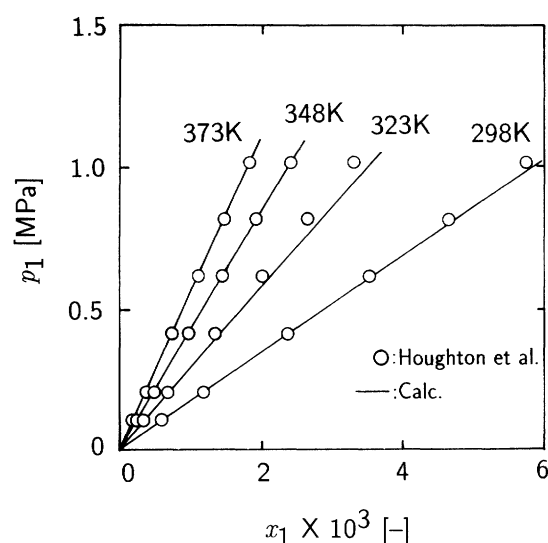
where the composition derivative of  $(n\alpha)$  can be calculated from the mixing rule. A detailed description of the equations including a procedure for the calculation of fugacity coefficient is given by Dahl and Michelsen<sup>5)</sup>.

For the modified UNIFAC model, the interaction parameters between three subgroups and three main groups have been determined by Larsen *et al.*<sup>13)</sup>. The group definitions for these groups together with the structural parameters  $R_k$  and  $(z/2) Q_k$ <sup>3)</sup> are listed in **Table 2**. The modified UNIFAC parameters  $a_{ij}$ <sup>13)</sup> were determined from the VLE data for the binary and the ternary systems in this work. The values of  $a_{ij}$  are shown in **Table 3**. In the temperature dependence of the interaction parameters in modified UNIFAC, we used only two terms,

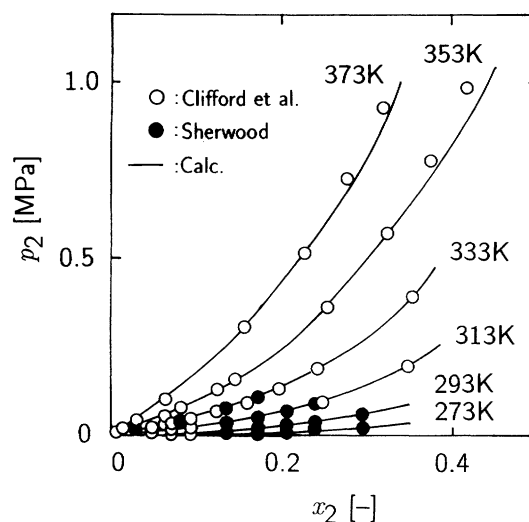
$$a_{ij} = a_{ij,1} + a_{ij,2} (T - T_0) \quad (7)$$

where  $T_0$  is a reference temperature,  $T_0 = 298.15\text{K}$ , and  $i$  and  $j$  represent the main groups.

## 2. Solubilities for CO<sub>2</sub> and NH<sub>3</sub> in H<sub>2</sub>O



**Fig. 1** Partial pressure vs. mole fraction of CO<sub>2</sub> for the CO<sub>2</sub>-H<sub>2</sub>O system. Experimental data by Houghton *et al.*<sup>9)</sup>

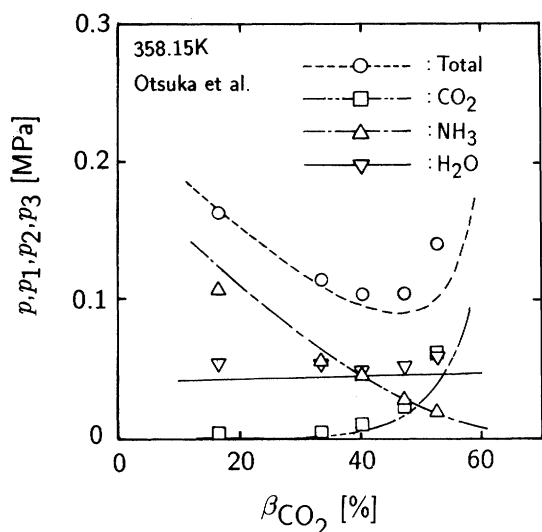


**Fig. 2** Partial pressure vs. mole fraction of NH<sub>3</sub> for the NH<sub>3</sub>-H<sub>2</sub>O system. Experimental data by Clifford *et al.*<sup>1)</sup> and Sherwood<sup>20)</sup>

### 2.1 Binary systems: CO<sub>2</sub>-H<sub>2</sub>O and NH<sub>3</sub>-H<sub>2</sub>O

First, VLE of the binary pairs CO<sub>2</sub> (1)-H<sub>2</sub>O (3) and NH<sub>3</sub> (2)-H<sub>2</sub>O (3) were correlated. Excellent agreement was obtained using the modified UNIFAC parameters as shown in Table 3, and as illustrated in **Figs. 1** and **2**.

The solubilities of CO<sub>2</sub> (1)-H<sub>2</sub>O (3) and NH<sub>3</sub> (2)-H<sub>2</sub>O (3) pairs could be successfully correlated by the SRK-EOS coupled with the MHV2 mixing rule employing the modified UNIFAC parameters  $a_{ij}$  of temperature dependence. Therefore, the application should be limited within  $1.87 \times 10^{-4} < x_{\text{CO}_2} < 5.74 \times 10^{-3}$  and  $298\text{K} < T < 373\text{K}$  for the CO<sub>2</sub> (1)-H<sub>2</sub>O (3) system and  $5.29 \times 10^{-3} < x_{\text{NH}_3} < 2.97 \times 10^{-1}$  and  $273\text{K} < T < 373\text{K}$  for the NH<sub>3</sub> (2)-H<sub>2</sub>O (3) system, respectively. It seems that chemical effects such as dissociation, hydration, and ion-ion long range interaction can be approximated effectively by adjusting the values of  $a_{ij}$  because the extent of dissociation of CO<sub>2</sub>



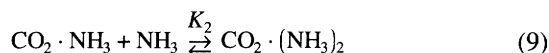
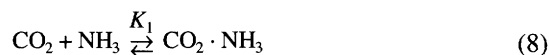
**Fig. 3** Total pressure and partial pressure of  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  vs.  $\beta_{\text{CO}_2}$  ( $= 100 \times (\text{wt.}\% \text{CO}_2 / (\text{wt.}\% \text{CO}_2 + \text{wt.}\% \text{NH}_3))$ ) for the  $\text{CO}_2$ - $\text{NH}_3$ - $\text{H}_2\text{O}$  system. (where  $p$ : Total,  $p_1$ :  $\text{CO}_2$ ,  $p_2$ :  $\text{NH}_3$ ,  $p_3$ :  $\text{H}_2\text{O}$ ) Experimental data by Otsuka *et al.*<sup>(17)</sup>

or  $\text{NH}_3$  in the aqueous phase is not so significant.

## 2.2 Ternary systems: $\text{CO}_2$ - $\text{NH}_3$ - $\text{H}_2\text{O}$

To correlate solubilities of the  $\text{CO}_2$  (1)- $\text{NH}_3$  (2)- $\text{H}_2\text{O}$  (3) ternary system, we need the binary parameters of  $\text{CO}_2$ - $\text{NH}_3$  pair,  $a_{12,k}$ . Therefore, we tried to find  $a_{12,k}$  to give a good fitting to experimental ternary solubilities<sup>(17)</sup>. However, no optimum values of  $a_{12,k}$  could be found. This indicates that the interaction between  $\text{CO}_2$  and  $\text{NH}_3$  in the aqueous phase is chemical rather than physical. Chemical effects, such as the carbamate formation reaction, should be taken into account.

In the present work, we assumed the following series reaction.



By representing the molalities in the aqueous phase as  $m_1$  ( $\text{CO}_2$ ),  $m_2$  ( $\text{NH}_3$ ),  $m_3$  ( $\text{H}_2\text{O}$ ),  $m_4$  ( $\text{CO}_2 \cdot \text{NH}_3$ ) and  $m_5$  ( $\text{CO}_2 \cdot 2\text{NH}_3$ ), respectively, the equilibrium constants are given as follows

$$K_1 = \frac{m_4}{m_1 m_2} \frac{\gamma_4}{\gamma_1 \gamma_2} \quad (10)$$

$$K_2 = \frac{m_5}{m_4 m_2} \frac{\gamma_5}{\gamma_4 \gamma_2} \quad (11)$$

where  $\gamma_4 = \gamma_1 \gamma_2$  and  $\gamma_5 = \gamma_4 \gamma_2$  are simply assumed. By assuming a series reaction, given by Eqs. (8) and (9), reasonable accuracy could be obtained, as shown in **Fig. 3**. In the present correlation the parameters  $A_i$  and  $a_{12,k}$  shown in Table 3 were determined simultaneously by fitting the calculated results to the experimental data cited in **Table 4**. The equilibrium constant is expressed by the following equation.

**Table 4** Mean absolute deviations in partial pressures of  $\text{CO}_2$  and  $\text{NH}_3$  calculated by the present model ( $K_1$  and  $K_2$ ) for the  $\text{CO}_2$ - $\text{NH}_3$ - $\text{H}_2\text{O}$  system

Temp. [K]	Molality		No. of Pts.	Comp.	Dev.* [%]	Ref.
	$\text{NH}_3$	$\text{CO}_2$				
373.15	7.4-2.9	1.8-0.5	8	$\text{CO}_2$	36.38	(17)
			8	$\text{NH}_3$	5.84	
353.15	8.7-3.1	2.0-0.5	10	$\text{CO}_2$	18.81	
			10	$\text{NH}_3$	4.30	
333.15	11.3-2.0	5.0-0.6	12	$\text{CO}_2$	47.89	
			12	$\text{NH}_3$	22.33	
313.15	15.3-2.2	5.6-0.6	11	$\text{CO}_2$	31.57	
			11	$\text{NH}_3$	7.19	
293.15	15.3-0.9	5.6-0.3	24	$\text{CO}_2$	28.09	
			24	$\text{NH}_3$	9.69	
333.15	2.3-0.5	1.5-0.3	19	$\text{CO}_2$	25.41	(12)
			19	$\text{NH}_3$	6.32	
313.15	2.2-0.5	1.1-0.3	3	$\text{CO}_2$	15.99	
			3	$\text{NH}_3$	4.33	
293.15	2.2-2.1	0.7-0.5	3	$\text{CO}_2$	5.05	
			3	$\text{NH}_3$	5.38	
373.15	9.6-3.1	5.4-0.9	8	$\text{CO}_2$	7.06	(18)
			8	$\text{NH}_3$	13.36	

\* Dev. [%] =  $100 \times |p_{i, \text{calc}} - p_{i, \text{exp}}| / p_{i, \text{exp}}$

**Table 5** Effect of temperature on equilibrium constants of chemical reactions (Eqs. (10) and (11))  
 $\ln K_i = A_1/T + A_2 \ln T + A_3 T + A_4$  ( $i = 1$  or  $2$ )

	$A_1$	$A_2$	$A_3$	$A_4$
$K_1$	$-1.628 \times 10^4$	3.253	-0.2372	115.4
$K_2$	$1.129 \times 10^4$	-5.872	0.1187	-39.08

$$\ln K_i = A_1 / T + A_2 \ln T + A_3 T + A_4 \quad i = 1 \text{ or } 2 \quad (12)$$

The values of  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$  are shown in **Table 5**. A summary of comparisons between calculated and experimental values is shown in Table 4. The present model can represent the solubility behavior of the  $\text{CO}_2$ - $\text{NH}_3$ - $\text{H}_2\text{O}$  system with reasonable accuracy.

## Conclusion

The solubility behavior of the  $\text{CO}_2$ - $\text{NH}_3$ - $\text{H}_2\text{O}$  ternary system can be correlated with reasonable accuracy using the SRK-EOS with the MHV2 mixing rule (physical effect) as the  $g^E$  mixing rule and by considering the series chemical reaction (chemical effect). It seems advantageous that solubility calculations for the  $\text{CO}_2$ - $\text{NH}_3$ - $\text{H}_2\text{O}$  system become simpler than other reasonable solution models. However, it is noted that the present model contains more physically unrealistic assumptions. Therefore, the application should be limited within  $m_{\text{CO}_2} < 5.6$  and  $m_{\text{NH}_3} < 15.3$  and  $293.15\text{K} < T < 373.15\text{K}$ .

This study shows the flexibility of the EOS with the  $g^E$  mixing rule to correlate solubilities of the  $\text{CO}_2$ - $\text{NH}_3$ - $\text{H}_2\text{O}$  system.

## Nomenclature

$a$	= constant of SRK-EOS	$[\text{m}^6 \cdot \text{Pa} \cdot \text{mol}^{-2}]$
$a_{ij}$	= interaction parameter for $i$ - $j$ interaction	$[\text{K}]$
$A_1$ - $A_4$	= coefficients in Eq. (17)	$[-]$
$b$	= constant of SRK-EOS	$[\text{m}^3 \cdot \text{mol}^{-1}]$
$C_1$ - $C_3$	= pure components temperature	

	dependence parameters	[-]
$g_0^E$	= molar excess Gibbs energy	[J·mol <sup>-1</sup> ]
$K$	= equilibrium constant	[kg·mol <sup>-1</sup> ]
$m$	= molality	[mol·kg <sup>-1</sup> ]
$M$	= molecular weight	[g]
$n$	= number of moles	[-]
$p$	= pressure	[Pa]
$p_i$	= partial pressure of component $i$	[Pa]
$(z/2) Q_k$	= surface area parameter	[-]
$q_1, q_2$	= mixing rule constants in Eq.(5)	[-]
$R$	= gas constant	[m <sup>3</sup> ·Pa·mol <sup>-1</sup> ·K <sup>-1</sup> ]
$R_k$	= volume parameter	[-]
$T$	= temperature	[K]
$T_0$	= reference temperature (= 298.15K)	[K]
$v$	= molar volume	[m <sup>3</sup> ·mol <sup>-1</sup> ]
$x$	= mole fraction	[-]
$\alpha$	= mixture parameter of SRK-EOS	[-]
$\beta$	= constant in Fig.3	[%]
$\phi$	= fugacity coefficient	[-]
$\gamma$	= activity coefficient	[-]
< Subscripts >		
1	= CO <sub>2</sub>	
2	= NH <sub>3</sub>	
3	= H <sub>2</sub> O	
4	= CO <sub>2</sub> ·NH <sub>3</sub>	
5	= CO <sub>2</sub> ·2NH <sub>3</sub>	
c	= critical property	
calc	= calculated value	
exp	= experimental value	
$i, j$	= components or groups $i$ and $j$	
mix	= mixture	
r	= reduced property	

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