

Calculation of H₂O-NH₃-CO₂ Vapor Liquid Equilibria at High Concentration Conditions

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Abstract A vapor liquid equilibrium model and its related interactive energy parameters based on UNIQUAC model for the H₂O-NH₃-CO₂ system without solid phase at the conditions of temperature from 30°C to 90°C, pressure from 0.1 MPa to 0.4 MPa, and the maximum NH₃ mass fraction up to 0.4 are provided. This model agrees with experimental data well (average relative error < 1%) and is useful for analysis of industrial urea production.

Keywords H₂O-NH₃-CO₂ system, vapor liquid equilibrium, high concentration, thermodynamic model

1 INTRODUCTION

H₂O-NH₃-CO₂ vapor liquid equilibria under high concentration conditions (NH₃ mass fraction is greater than 0.2 in liquid phase) and the thermodynamic model are necessary for simulation, analysis and optimization of industrial urea processes.

In the respect of vapor liquid equilibrium thermodynamic models, the theory of strong electrolyte were introduced into H₂O-NH₃-CO₂ system^[1-3], which covered the range of mass fraction of NH₃ up to 0.15. Subsequently, Bernardis *et al.*^[4] applied UNIQUAC equation to calculating H₂O-NH₃-CO₂ vapor liquid equilibria at the temperature of 100°C, which corresponded to mass fraction of NH₃ up to 0.25. But all of those models did not meet the need of urea process simulation, especially for circulating absorption system with high NH₃ and CO₂ concentrations. Up to now, thermodynamic model about H₂O-NH₃-CO₂ vapor liquid equilibrium under high concentration conditions was not reported.

In this paper, the relations of H₂O-NH₃-CO₂ vapor liquid equilibria and UNIQUAC interaction energy parameters are presented based on method reported in the literature^[1,2,4].

2 UNIQUAC INTERACTIVE ENERGY PARAMETERS

In the UNIQUAC model^[5] for electrolyte solu-

tions, the Debye-Huckel activity coefficient γ^{DH} reflecting electrical charges and the form-structure activity coefficient γ^{C} reflecting the particle volume and surface area just contain characteristic constants of each component, only the interactive energy parameters $a_{i,j}$ (i, j stand for components in solution) in excess energy activity coefficient γ^{R} are related to specific systems composed of different species.

In liquid phase of the H₂O-NH₃-CO₂ system in which crystallization does not take place, there are five reactions^[1] creating nine species: H₂O(1), NH₃(2), CO₂(3), NH₄⁺(4), HCO₃⁻(5), CO₃²⁻(6), NH₂COO⁻(7), OH⁻(8), and H⁺(9). We find that the model precision can be improved substantially when a temperature coefficient is applied to $a_{i,j}$. In this model, temperature ranges from 30–90°C, the linear function is found to be the best

$$a_{i,j} = \alpha_{i,j} + \beta_{i,j}t \quad (1)$$

In Eq. (1), $\alpha_{i,j}$ and $\beta_{i,j}$ are temperature coefficients of interaction energy parameters $a_{i,j}$, t is temperature in °C. $\alpha_{i,j}$ and $\beta_{i,j}$ are shown in Tables 1 and 2 separately.

3 THE RELATIONS OF VAPOR LIQUID PHASE EQUILIBRIA

Vapor liquid equilibria in the H₂O-NH₃-CO₂ system indicate that the fugacities of H₂O, NH₃, and

Table 1 Temperature coefficient of interaction energy parameter, $\alpha_{i,j}$

i	j								
	1	2	3	4	5	6	7	8	9
1	0	-452.48	478.41	555.15	135.01	559.81	661.56	751.25	612.29
2	266.62	0	-1227.89	1177.28	607.98	58.54	1146.17	-771.32	-64.32
3	513.30	-403.91	0	-318.17	-422.83	-521.24	-272.81	-884.29	-372.72
4	-475.51	449.58	-302.06	0	-99.76	-620.00	-1190.53	411.57	-603.63
5	400.85	254.48	-312.08	-160.09	0	-432.75	-173.55	-609.37	-670.79
6	-552.88	523.30	-629.88	-343.16	-375.90	0	-646.29	194.79	-725.29
7	-234.44	548.35	-247.41	-164.68	-39.87	-489.01	0	552.05	-315.85
8	730.93	-774.35	-883.20	537.45	756.29	532.29	603.05	0	1.52
9	129.91	-7.44	-347.84	-605.07	-675.79	-607.54	18.29	10.62	0

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Table 2 Temperature coefficient of interaction energy parameter, $\beta_{i,j}$

<i>i</i>	<i>j</i>								
	1	2	3	4	5	6	7	8	9
1	0	3.41	0.40	7.22	3.19	-3.10	-6.20	0	0
2	-0.77	0	7.30	-5.30	-2.00	9.25	-7.50	0	0
3	-7.70	8.20	0	-2.70	-4.45	-4.45	7.72	0	0
4	-1.89	-7.10	3.08	0	-4.68	0.32	9.70	0	0
5	-7.90	-0.70	-5.20	-7.31	0	-4.71	6.74	0	0
6	8.70	-1.60	-3.34	-3.99	-5.19	0	7.60	0	0
7	-0.18	-8.50	7.90	-5.80	-0.38	3.10	0	0	0
8	0	0	0	0	0	0	0	0	0
9	0	0	0	0	0	0	0	0	0

CO₂ in vapor phase are equal respectively to that of free H₂O, NH₃, and CO₂ in liquid phase. The vapor liquid equilibrium relationship of component H₂O is reasonably described by the modified Raoult's equation. In the H₂O-NH₃-CO₂ liquid solution, as the composition of free CO₂ is very low and the composition of free NH₃ is sometimes very high according to its mass composition and the ratio of NH₃ to CO₂^[1,2], so the modified Henry's equation is chosen for CO₂ and the modified Raoult's equation for NH₃ under high liquid concentration condition.

For component H₂O(1) and component NH₃(2)

$$y_i \varphi_i p = x_i \gamma_i \varphi_i^s p_i^s \exp \left[\frac{(p - p_i^s) v_i}{RT} \right], i = 1, 2 \quad (2)$$

and for component CO₂(3)

$$y_3 \varphi_3 p = x_3 \gamma_3 H_3 \exp \left[\frac{(p - p_1^s) v_3}{RT} \right] \quad (3)$$

where *y* is vapor mole fraction, φ is fugacity coefficient, *p* is pressure in MPa, *x* is liquid mole fraction, γ is activity coefficient, *H* is Henry constant in MPa, *v* is the specific liquid volume of component in cm³·mol⁻¹, *R* is ideal gas constant 8.31434 J·mol⁻¹·K⁻¹, and *T* is temperature in K.

The relationship of volume *v_i* and temperature is

$$v = E_1 + E_2 t + E_3 t^2 \quad (4)$$

where *t* is temperature in °C. Temperature coefficients *E* is shown in Table 3.

Table 3 Temperature coefficients of volume parameter^[2]

	<i>E</i> ₁	<i>E</i> ₂	<i>E</i> ₃	Temperature range, °C
<i>v</i> ₁	18.01	0.0180	0.00112	0—150
<i>v</i> ₂	28.68	0.0036	0.00048	20—160
<i>v</i> ₃	32.42	0.0023	0.00057	0—150

The relation of Henry's coefficient of CO₂(3) and temperature is

$$\ln(H) = B_1/T + B_2 \ln T + B_3 T + B_4 \quad (5)$$

and the temperature coefficient *B* is in Table 4.

Table 4 Temperature coefficient of Henry's coefficient of CO₂^[4]

<i>B</i> ₁	<i>B</i> ₂	<i>B</i> ₃	<i>B</i> ₄	Temperature range, °C
-17060.70	-68.3159	0.065989	431.9060	0—200

Table 5 Calculated data and corresponding literature data^[6] of H₂O-NH₃-CO₂ VLE

Temp. °C	Pres. MPa	Liquid mass percent, %				Vapor mass percent, %					
		CO ₂	NH ₃			NH ₃			CO ₂		
			Lit.	Cal.	Err.	Lit.	Cal.	Err.	Lit.	Cal.	Err.
30	0.101	20.0	30.0	29.54	0.46	97.5	97.39	0.11	0.1	0.10	0
	0.196	20.0	37.5	38.27	-0.77	99.0	99.09	-0.09	0.03	0.02	0.01
40	0.101	20.0	26.5	25.56	0.94	94.0	94.39	-0.39	1.0	0.72	0.28
	0.101	25.0	27.5	27.19	0.31	94.0	94.47	-0.47	1.1	0.89	0.21
	0.196	20.0	32.8	32.93	-0.13	97.5	97.92	-0.42	0.10	0.13	-0.03
	0.196	25.0	33.5	33.39	0.11	97.6	97.97	-0.37	0.15	0.14	0.01
50	0.29	25.0	34.2	33.95	0.25	97.2	97.62	-0.42	0.50	0.30	0.20
	0.29	30.0	35.5	34.80	0.70	97.4	97.71	-0.31	0.60	0.35	0.25
	0.39	20.0	37.6	37.68	-0.08	98.3	98.53	-0.23	0.15	0.12	0.03
	0.39	25.0	37.8	37.82	-0.02	98.3	98.56	-0.26	0.20	0.14	0.06
60	0.29	25.0	30.5	30.33	0.17	94.7	94.66	0.04	1.61	1.57	0.04
	0.29	30.0	32.0	31.84	0.16	95.0	94.61	0.39	1.80	1.92	-0.12
	0.39	25.0	34.0	33.83	0.17	96.5	96.82	-0.32	0.86	0.70	0.86
	0.39	30.0	35.0	34.81	0.19	96.7	96.88	-0.18	1.01	0.82	0.19
70	0.29	30.0	29.3	29.00	0.30	85.2	85.42	-0.22	10.2	9.01	1.16
	0.29	35.0	31.3	31.46	0.16	83.2	83.70	-0.50	12.7	11.49	1.24
	0.39	30.0	31.8	31.98	-0.18	91.2	92.26	-1.06	5.00	3.87	1.13
	0.39	35.0	34.0	33.99	-0.01	90.9	91.90	-1.00	5.58	4.71	0.87
80	0.29	25.0	23.2	23.20	0	69.2	66.18	3.02	22.8	24.82	-2.02
	0.29	30.0	24.6	24.79	-0.19	58.0	53.46	4.54	35.6	39.18	-3.58
	0.39	25.0	27.2	27.09	0.11	81.0	82.13	-1.13	12.5	11.20	1.30
	0.39	30.0	29.0	29.03	-0.03	78.0	78.40	-0.40	16.2	15.76	0.46
90	0.39	20.0	22.0	21.79	0.21	65.0	66.98	-1.98	24.5	22.26	2.24
	0.39	25.0	23.0	22.62	0.38	53.0	53.12	-0.12	38.5	37.94	0.56
Ave.					0.251			0.749			0.702

The fugacity coefficients of vapor components are calculated using BWRS equation of state.

4 RESULT AND DISCUSSION

Part of calculated data and corresponding literature data of the H₂O-NH₃-CO₂ vapor liquid equilibrium system is listed in Table 5.

The ternary-two-phase H₂O-NH₃-CO₂ system has three degrees of freedom. When temperature and pressure are fixed, CO₂ mass percentage in liquid phase is chosen as the third variable. So NH₃ mass fraction in liquid phase and vapor compositions are to be calculated.

The average absolute error of NH₃ mass percentage in liquid phase is 0.251%, and this accuracy is very beneficial to the process simulation of H₂O-NH₃-CO₂ vapor condensation.

The average absolute error of NH₃ in vapor phase is 0.749% and that of CO₂ mass percent in vapor

phase is 0.702%. This agreement with literature data is very satisfactory.

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Note: An appendix containing the detailed description on the electrolytic equilibrium and the UNIQUAC equations with parameters may be available by communicating with email to the editorial department.