Estimation of UNIQUAC-NRF Model Parameters for NH$_3$-CO$_2$-H$_2$O System

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ABSTRACT: *Vapor-liquid equilibrium in NH3-CO2-H2O system at high pressures has been studied. The UNIQUAC-NRF model for this system was extended by using the Goppert 4 maurer reported datas. Since the system contains molecules and ionic species the binary interaction parameters considered, where those are of molecule-molecule, molecule-ion and ion-ion types. These interaction parameters are taken as constant values in UNIQUAC-NRF, which are not accurate. In this work the mentioned parameters have been considered as function of temperature in quadratic form. By applying an optimization mathematical program to the UNIQUAC-NRF model and experimental data reported by Goppert and Maurer the model parameters were obtained in term of temperature. The results of this model with the new parameters show good agreement with experimental data.*

INTRODUCTION

The solubility data of gaseous in liquids are frequently used in gas-treating processes design and it can be calculated from the vapor-liquid equilibrium (VLE) data. The VLE in aqueous solutions of electrolyte are encountered in variety of fields such as waste water, biogas production and oil recovery. A thermodynamic model describing such equilibrium can therefore be of great use for designing and optimizing processes in these fields. Van Krevelen et al. proposed a model based on equilibrium and Henry's law Coefficients [1]. Edwards et al. used an extended form of the Debye-Huckel law for the liquid phase activity coefficients, and the Virial equation of state for the pure component fugacity of each

component in the vapor phase [2, 3]. Vega and Vera proposed a model for calculation of liquid phase activity coefficients with a semi-empirical equation for aqueous solutions containing volatile strong electrolytes [4]. Cruz and Renon calculated the activity coefficients with the NRTL model for binary systems in weak electrolyte solution [5], [6]. Chen and Evans applied the NRTL model for prediction of mean ionic activity coefficient of binary systems and calculated the vapor phase fugacity coefficients with the SRK equation of state [7]. Rumpf and Maurer [8] and Clegg and Brimblecombe [9] modeled the vapor-liquid equilibrium using the Pitzer model [10]. Bernardis et al. extended the UNIQUAC

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model for NH_3-CO_2-H_2O with the equation of state suggested by Nakamura et al. [1] for the vapor phase [12].

Haghtalab and Asadollahi [13] proposed the UNIQUAC-NRF model to calculate the activity coefficients of components such as molecules and ions with Peng-Robinson equation of state for vapor phase. In this work the UNIQUAC - NRF model parameters were calculated by using of Goppert and Maurer [14] experimental data for NH3-CO2-H2O system.

THE NH_3-CO_2-H_2O SYSTEM

The vapor-liquid equilibrium in the NH_3-CO_2-H_2O ternary system is shown in Fig. 1. The gas phase contains NH_3, CO_2 and water in molecular form and the liquid phase contains NH_3 and CO_2 not only in molecular, but also in ionic form. In this system, nine distinct species exist: NH_3, CO_2, H_2O, NH_4^+, HCO_3^-, $CO3^{2-}$, H^+, OH^- and NH_2COO^-. These species and their relevant reaction has been presented in Fig. 1. It is assumed that the dissociation of NH_3 and H_2O, the first and second, dissociation of CO_2 a long with formation of carbonate are the most important chemical reactions in predicting the equilibrium state of this system.

THE UNIQUAC-NRF MODEL

The UNIQUAC-NRF model is used to calculate the activity coefficients in multicomponent mixture, base on molar excess Gibbs energy. In this model the same assumptions of NRTL-NRF model, were presented by Vera[14], are used. This model is based on the existence of different types of cells. Two types of cells are those with a cation or with an anion as central species and other cells are solvent cells. For ionic cells, the like ion repulsion leads to the assumption that the local area fraction of cation around cation and anion around anion is zero. Thus, only solvents and counter ion species surround one particular ion. The third type of cell has solvents with anions (cations) as ascentral molecules and solvent molecules in the surrounding.

The activity coefficients of components in a mixture can be calculated as below:

$$\ln \gamma_i = \left[\frac{\partial (n_i g^{ex}/RT)}{\partial n_i} \right]_{T,P,n_{j \neq i}} \qquad (1)$$

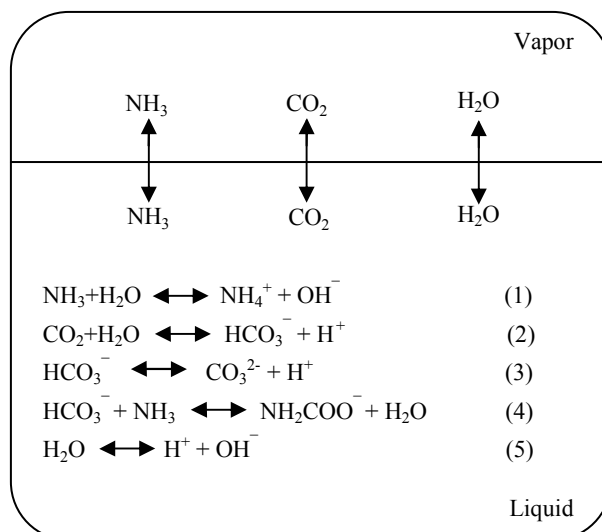in which g^{ex} is excess Gibbs energy that expressed as:

Fig. 1: Vapor-liquid equilibrium and chemical reactions in the NH_3-CO_2-H_2O system.

$$g^{ex} = (g^{ex})_c + (g^{ex})_R \qquad (2)$$

where C and R indicate the combinatorial and residual parts of reaction between species that presented by Haghtalab and Asadollahi [13]. Finally activity of componential mathematically can be expressed as:

$$\ln (ai)_{\text{UNIQUAC-NRF}} = \ln \phi_i + \frac{z}{2} q_i \qquad (3)$$

$$\ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^{n} x_j l_j + \ln \gamma_i^R$$

where

$$\ln \gamma_i^R = q_i \left[1 + \ln \Gamma_{ii} - \sum_{\substack{j=i \\ j \neq i}}^{n} \theta_j \Gamma_{ij} + (1 - \theta_j) \sum_{\substack{j=i \\ j \neq i}}^{n} \theta_j \ln \left(\frac{\Gamma_{ij}\Gamma_{ji}}{\Gamma_{ii}\Gamma_{jj}} \right) - \right.$$

$$\left. \frac{1}{2} \sum_{\substack{k=l \\ k \neq l}}^{n} \sum_{\substack{l=l \\ l \neq k \\ l \neq i}}^{n} \theta_k \theta_l \ln \left(\frac{\Gamma_{lk}\Gamma_{kl}}{\Gamma_{ll}\Gamma_{kk}} \right) \right]$$

$$l_i = l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$$

$$\Gamma_{ij} = \tau_{ij}.\Gamma_{jj} \qquad \tau_{ij} = \exp \left(\frac{-a_{ij}}{RT} \right)$$

in which r and q are the pure parameters of i species, a_{ij} and τ_{ij} are the energy of interaction and interaction parameters of i-j pairs, respectively. The only adjustable

parameters of the model are the binary interaction parameters. A discussion of the physical significance and importance of these parameters can be found in reference [13].

EVALUATION OF PARAMETERS

The adjustable parameters of the model, "a_{ij} , a_{ji}", are assumed to be independent of temperature at low pressure as give by Haghtalab and Asadollahi [13].

These parameters are related to the energy of interaction between the species, so it is not suitable to be taken as a constant. In this work some of these parameters are assumed to be temperature dependent and were fitted to the following second order equation as a function of temperature:

$$a_{ij} = \alpha_{ij} + \beta_{ij}T(K) + \delta_{ij}T^2(K) \qquad (4)$$

$$a_{ji} = \alpha_{ji} + \beta_{ji}T(K) + \delta_{ji}T^2(K) \qquad (5)$$

The best values of α, β, δ were determined by minimizing the following objective function:

$$O.F. = \sum_i^N \left[\frac{P^{cal} - P^{exp}}{P^{exp}} \right]_i^2 + \left[\frac{P_{NH_3}^{cal} - P_{NH_3}^{exp}}{P_{NH_3}^{exp}} \right]_i^2 + \\ \left[\frac{P_{CO_2}^{cal} - P_{CO_2}^{exp}}{P_{CO_2}^{exp}} \right]_i^2 \qquad (6)$$

where N, P_{NH3} and P_{CO2} are number of data points, partial pressure of NH3 and partial pressure of CO_2, respectively. The number of binary parameters in considered system, (NH$_3$-CO$_2$-H$_2$O), with nine species in solution are 81. Actually some of the interactions are set equal to zero, such as cation-cation, anion-anion and self interactions , and some other parameters have no influence on calculations. The binary interaction for NH$_3$-H$_2$O and CO$_2$-H$_2$O systems were calculated from the relation ship given by Houghton et.al. [16] simply as a function of temperature, as:

$$a_{ij} = AT + B \qquad (7)$$

where A and B were obtained by minimization of the following objective functions:

$$O.F._P = \sum_i^N \left(P_i^{exp} - P_i^{cal} \right)^2 \qquad (8)$$

$$O.F._y = \sum_i^N \left(y_i^{exp} - y_i^{cal} \right)^2 \qquad (9)$$

The other binary interaction between molecule-ion and ion-ion that assumed in this work calculated as a function of temperature from experimental data that has been reported by Goppert and Maurer[14] in temperature range equal to 353.15-393.15K by minimizing the mentioned objective function.

RESULTS AND DISCUSSION

The activity coefficient as function of temperature by equation (4) and (5) for binary molecule-ion pair and ion pair-molecule interaction parameters are reported. The complete system of governed equations for calculating the vapor-liquid phase equilibrium data like partial pressure of components in vapor phase of a ternary system can be found elsewhere (Haghtalab and Asadollahi) [13]. The partial pressure data of CO2 and NH3 in "carbon dioxide, ammonia and water" system at various concentration reported by Goppert and Maurer [14] were used as base for emperature dependent interaction terms in UNIQUAC-NRF model in this study. Within 81 interaction parameters for nine species involved in considered system, some don't have significant on phase equilibrium and only some parameters are with importance influence in calculation which have been taken as function of temperature. A number of those parameters are considered as simple function of temperature, like molecule – molecule pair binary interaction of NH$_3$-H$_2$O and CO$_2$-H$_2$O systems as shown in table 2.

The energy of interaction a_{ij} for ion-molecule and ion-ion obtained as a function of temperature, in form of quadratic polynomial with three constant parameters α, β, δ, Eq. (4) and (5) by using an optimization program to fit the experimental data with UNIQUAC-NRF model at temperature range of 353.15 K-393.15K. The obtained parameters have been presented in Table 3.

The pure parameters r_i and q_i reported by Thomson and Rasmussen [17] , [18] ,presented in table 4, were used in calculation of activity coefficients.

For 240 experimental data, the root mean squared deviation (RMSD) between experimental and calculated

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Table 2: The binary interaction of NH₃-H₂O and CO₂-H₂O systems.

i	J	α_{ij}	α_{ji}	AAD%	Reference
NH_3	H_2O	2.8312T-1.12e-5	1.5504T+7.8e-8	3.5 (1)	[23]
CO_2	H_2O	2.2385T-254.0429	0.001T	1.17 (2)	[24]

$$(1):\frac{1}{N}\sum_{i}^{N}\left|\frac{y_i^{exp}-y_i^{cal}}{y_i^{exp}}\right|\times100 \qquad ; \qquad (2):\frac{1}{N}\sum_{i}^{N}\left|\frac{P_i^{exp}-P_i^{cal}}{P_i^{exp}}\right|\times100$$

Table 3: The value of different parameters by applying equation (4) and (5) for binary interactions base on UNIQUAC-NRF model.

I	J	α_{ij}	β_{ij}	δ_{ij}	α_{ji}	β_{ji}	δ_{ji}
NH_4^+	H_2O	-11895.985	58.098	-0.0737	-16816.378	89.917	-0.1128
NH_2COO^-	H_2O	-8385.409	43.211	-0.057	-21765.391	115.838	-0.1452
HCO_3^-	H_2O	-10265.763	49.704	-0.0628	-5008.8049	24.331	-0.0307
NH_3	NH_4^+	-63841.456	344.1	-0.4366	-2626.8742	12 986	-0.0166
NH_3	NH_2COO^-	-38135.701	203.405	-0.2516	-9368.0694	45.853	-0.0581
CO_2	NH_4^+	-9178.109	45.093	-0.0573	-25020.599	133.189	-0.162
CO_2	NH_2COO^-	-22836.761	111.942	-0.1418	-8957.851	47.769	-0.0598
CO_2	HCO_3^-	-5600.995	27.477	-0.0349	-19338.637	94.99	-0.1206
NH_4^+	NH_2COO^-	-32005.311	170.993	-0.2059	-4035.748	21.371	-0.0268
NH_4^+	HCO_3^-	-30773.108	164.283	-0.2024	-21209.284	112.488	-0.1387

Table 4: UNIQUAC-NRF, surface parameter a r and q parameters fitted to experimental data for each component containing molecules and ions[17], [18].

	H_2O	NH_3	CO_2	NH_4^+	HCO_3^-	CO_3^{2-}	NH_2COO^-	H^+	OH^-
r	0.92	1.439	5.741	4.815	8.075	10.828	4.375	0.137	9.397
q	1.4	2.091	6.08	4.602	8.68	10.762	5.135	10^{-5}	8.817

Table 5: The results of RMSD of pressure and vapor mole fraction by applying UNIQUAC-NRF model with new parameters.

UNIQUAC-NRF model	RMSD(P)%	RMSD(y_i)%
With fixed parameters	8.9	11.8
With new parameters	7.8	9.51

* Calculated by Bernardis et al. [12]

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pressures datas, and vapor mole fractions base on UNIQUAC-NRF model with new temperature dependent parameters, reported in table 5. The presented percentage deviation in this table shows improvement in RMSD%, of about 16%, for model with new parameters, so the coefficients of equation (4) and (5) for binary interaction parameters were found to be highly correlated.

The experimental data of total pressure against the CO_2 molality for several different concentration of NH_3 and the results of UNIQUAC-NRF model with applying new temperature dependence interaction parameters in temperature range of 353.15-360.15K are shown in Fig. 2. The pressure curves generated by the model in this figure exhibit interesting agreement between experimental data and those predicted by the model.

CONCLUSION

Phase behavior of NH_3-CO_2-H_2O system for 240 experimental data were used to obtain the binary interaction parameters of UNIQUAC-NRF model as a function of temperature. The UNIQUAC-NRF model was further extended for this system (NH_3-CO_2-H_2O) by presenting the new model parameters. Some binary interaction parameters determined from optimization of difference between experimental and calculation data for binary VLE data. The binary interaction parameters for ion-ion and ion-molecule were considered temperature dependent in from of second order polynomial function. The results of RMSD for total pressure and vapor mole fraction of the correlation VLE data show that the predicted data by the UNIQUAC-NRF model with new binary parameters has good agreement with experimental data. The model with use of new parameters predicts the VLE data for CO2-NH3-H2O system better, about 16% , than the previous model.

List of Symbols

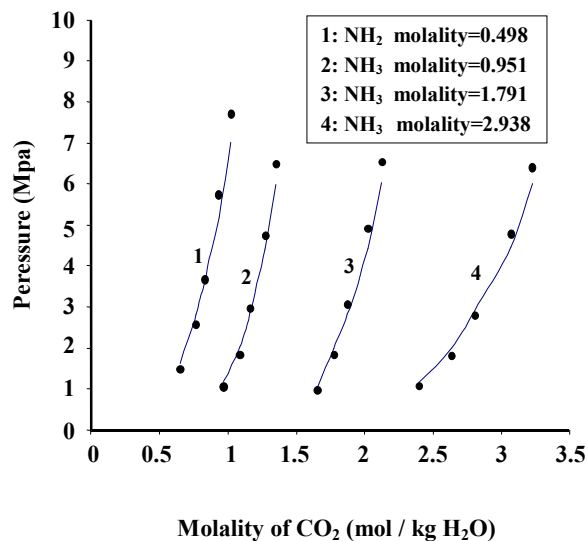|	
a_i	Activity of component
a_{ij}	Interaction parameter between component i and component j
AAD	Absolute average deviation
A	Coefficient in equation (7)
B	Coefficient in equation (7)
l	Size parameter in UNIQUAC equation
g^{EX}	Excess Gibbs free energy
n	Molecular weight of solvent

Fig. 2: Comparison between experimental and calculated data of total pressure vs. molality of CO_2 at 353.15K for different concentration of NH_3; (-) results of the UNIQUAC-NRF model with new parameters; (●) experimental data reported in reference [14].

N	Number of experimental points
O.F.	Objective Function
P	Pressure
q	Surface parameter
r	Volume parameter
RMSD	Root Mean Square Deviation
T	Absolute temperature
x	Liquid mole fraction
y	Vapor mole fraction
Z	Coordination number

Greek Letters

γ	Activity coefficient
Γ	Nonrandom factor
φ	Volume fraction
θ	Surface fraction
τ	Interaction parameter

Subscripts

i,j	Component
n	Solvent
C	Combinatorial
R	Residual

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Superscripts

R   Residual
cal   Calculated value
exp   Experimental value

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