NH_3-CO_2-H_2O VLE Calculation Using an Extended UNIQUAC Equation

M. Bernardis
G. Carvoli
P. Delogu
Istituto Guido Donegani S.p.A.
I-28100 Novara, Italy

NH_3-CO_2-H_2O vapor-liquid equilibrium (VLE) is extensively treated in literature, both experimentally and theoretically. However, as Maurer (1986) clearly pointed out, thus far no satisfactory model describing such a system in a large range of composition and temperature has been found.

The main purpose of this paper is to calculate the activity coefficients of the components, applying an extended UNIQUAC equation, as originally proposed by Sander et al. (1986 a, b, c) to solve several complex VLE equations involving electrolytes.

The UNIQUAC equation seems to solve particularly difficult phase equilibrium problems. In fact, the combinatorial term coupled with the residual term containing the local molar mixing rule, gives rise to a remarkable flexibility in fitting data. Moreover, the UNIQUAC equation allows the addition of new components without refitting the interaction parameters already obtained for components previously treated. On the other hand, the UNIQUAC equation permits consideration of water in the same way as the other components, i.e., with its own interaction parameters. In other models, like Pitzer's model (Pitzer, 1973), the excess free energy is built up without using water interaction parameters. This causes a certain stiffness, especially when the model is extended to new components.

Thermodynamic Framework

The vapor fugacity, f_i^v, of a generic component, i, is expressed, as usual, by the following equation:

$$f_i^v = P y_i \phi_i \tag{1}$$

where P is the pressure in MPa; y_i and ϕ_i are, respectively, the vapour mole fraction and the fugacity coefficient of component i.

In the case concerning NH_3, CO_2, and H_2O, we use Nakamura's equation of state (Nakamura, 1976) to calculate the fugacity coefficients. The liquid fugacity, f_i^L, where i could be NH_3 or CO_2, follows from:

$$f_i^L = H_i^{(P)} a_i^{\nabla} = H_i^{(P)} m_i \gamma_i^{\nabla} \tag{2}$$

a_i^{∇} being the liquid activity equal to the product of the true liquid molality, m_i (mole/kg of water) and the asymmetric liquid activity coefficient, γ_i^{∇}, on a molality scale. $H^{(P)}$ is Henry's constant, explicable as:

$$\ln H_i^{(P)} = \ln H_i^{(P_w^s)} + V_i^{\infty} (P - P_w^s)/RT \tag{3}$$

where $\ln H_i^{(P_w^s)}$ is equal to:

$$\ln H_i^{(P_w^s)} = B_1/T + B_2 \ln T + B_3 T + B_4 \tag{4}$$

The constants B_1, B_2, B_3, and B_4, for NH_3 and CO_2, appear in Table 1 and are obtained by the procedure shown in the paragraph, "Estimation of Parameters"; P_w^s is the saturation pressure of water; V_i^{∞} is simply calculated as suggested by Edwards et al. (1978). The fugacity of liquid water is:

$$f_w^L = f_w^o a_w = f_w^o x_w \gamma_w \tag{5}$$

where a_w is the liquid activity of water, x_w the true liquid mole fraction, and γ_w the symmetric liquid activity coefficient. The pure water fugacity, f_w^o, is always calculated via Nakamura's equation of state. Finally, because of the chemical reactions occurring in solution, m_i and x_w are not stoichiometric quantities, as shown in the next paragraph.

Chemical Reactions in Solution

We consider the following chemical reactions occurring in solution: the dissociation of water, ammonia and carbon dioxide, and carbamate formation, producing the five ionic species

---

Correspondence concerning this paper should be addressed to G. Carvoli.

Table 1. Henry's Constants as a Function of Temperature*

Electrolyte	B_1	B_2	B_3	B_4	Applicability Range (K)
NH_3	−681.531	28.67202	−0.0541721	−151.3689	273-423
CO_2	−8,901.728	−22.198746	0.0018684	156.8758	273-423

*$\ln H^{(P_w)} = B_1/T + B_2 \ln T + B_3 T + B_4$
$H^{(P_w)}$ = kg MPa/mol; T = K

NH_4^+, HCO_3^-, NH_2COO^-, H^+, and OH^-. These species, not present in the vapour phase, play a fundamental role, whether in the expression of the liquid activity coefficient or in the mass and electroneutrality balances.

Usually the bicarbonate ion dissociation is taken into account (Edwards et al., 1978). However, we found our calculations independent from carbonate ion concentration, always very low because of the small value of the equilibrium thermodynamic constant. For this reason, we ignored such a reaction. The equilibrium thermodynamic constants were taken from Pawlikowski et al. (1982).

Activity Coefficient Expression

We will follow Sander et al. (1986b) by using an extended UNIQUAC equation to describe the liquid nonideality of the system NH_3-CO_2-H_2O. It is convenient to choose the asymmetric convention on a molar scale (star marked) to represent the activity coefficients of ions NH_3 and CO_2. (The symmetric convention is chosen for water.) These ions are related to asymmetric convention on a molality scale as follows:

$$\ln \gamma_i^{\nabla} = \ln \gamma_i^* + \ln x_w \tag{6}$$

Furthermore, the activity coefficients are divided into three parts:

$$\ln \gamma_w = \ln \gamma_w^{DH} + \ln \gamma_w^C + \ln \gamma_w^R \tag{7}$$

$$\ln \gamma_i^* = \ln \gamma_i^{*,DH} + \ln \gamma_i^{*,C} + \ln \gamma_i^{*,R} \tag{8}$$

where DH means Debye-Hückel; C, combinatorial; and R, residual. The explicit expressions of individual parts are shown in the reference, Sander et al. (1986b).

Estimation of Parameters

In solutions, eight species are taken into account: NH_3, CO_2, NH_4^+, HCO_3^-, NH_2COO^-, H_2O, H^+, and OH^-. Therefore, the interaction parameters,a_{kl}, appearing in Eqs. 45 and 46 of Sander et al. (1986b), are 64. Actually, some interactions are set equal to zero (cation-cation, anion-anion, and self-interactions), and others have no influence on calculations. The final set of interaction parameters and the literature references of experimental data appear in Table 2.

It should be noted that only the interaction parameters regarding the couples NH_3-H_2O and CO_2-H_2O are temperature-dependent. These were estimated together with the Henry's constants from binary systems only, as shown in Table 2; all the other interaction parameters were obtained from ternary VLE data at one temperature only: 373.15 K. The pure component parameters, r_i, and q_i, appearing in Eqs. 42 and 43 of Sander et al. (1986b) were determined following the procedure of the cited authors.

Results and Discussion

In Figure 1 are shown the experimental ternary data used to optimize interaction parameters, compared with the calculated curves obtained from the best parameters set reported in Table 2. For 171 data points, the root mean squared deviation between experimental and calculated pressures is 8.90%; between experimental and vapor mole fractions, 11.81%. More interesting is

Table 2. Interaction Parameters Values: P, T and Molality Range of Experimental Determinations Used to Estimate Parameters

i	k	a_{ik}	a_{ki}	Remarks	References
Experimental Source: Binary VLE Data					
NH_3	H_2O	4,969.77 $-20.83235T$ $+0.0188211T^2$	−25,642.10 $+107.7931T$ $-0.1086847T^2$	T = 373.15 − 503.15 K P = 0. − 9.0 MPa m_{NH_3} = 0.0 − 452.7	Guillevic et al. (1985) Pawlikowski et al. (1982)
CO_2	H_2O	−1,272.667 $+183{,}114.45/T$	2,282.919 $-334{,}031.43/T$	T = 273.15 − 373.15 K P = 0. − 3.75 MPa m_{CO_2} = 0.0 − 1.5	Houghton et al. (1957)
Experimental Source: Ternary VLE Data					
NH_4^+	H_2O	−797.8	646.5		
NH_2COO^-	H_2O	−330.3	800.5	T = 373.15 K	
HCO_3^-	H_2O	−772.5	−474.4		
NH_3	NH_4^+	2,500.0	−154.0	P = 0. − 0.87 MPa	
NH_3	NH_2COO^-	2,500.0	−657.0		Göppert and Maurer (1988)
CO_2	NH_4^+	−634.0	1,335.2	m_{NH_3} = 0.0 − 18.4	
CO_2	NH_2COO^-	−1,026.5	217.7		
CO_2	HCO_3^-	−394.9	−1,061.5	m_{CO_2} = 0.0 − 9.7	
NH_4^+	NH_2COO^-	2,500.0	−62.5		
NH_4^+	HCO_3^-	1,766.5	983.7		

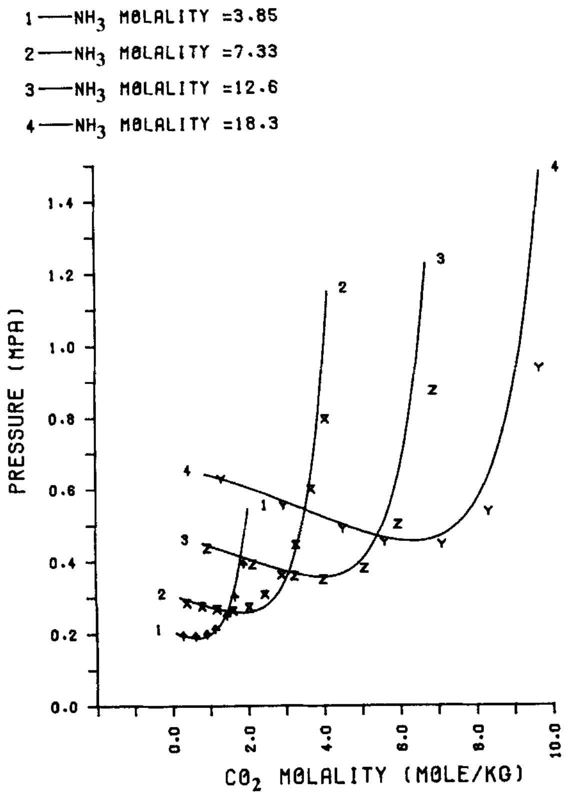

Figure 1. Optimized curves vs. experimental points: total pressure vs. CO_2 molality at 373.15 K and at different ammonia molalities.

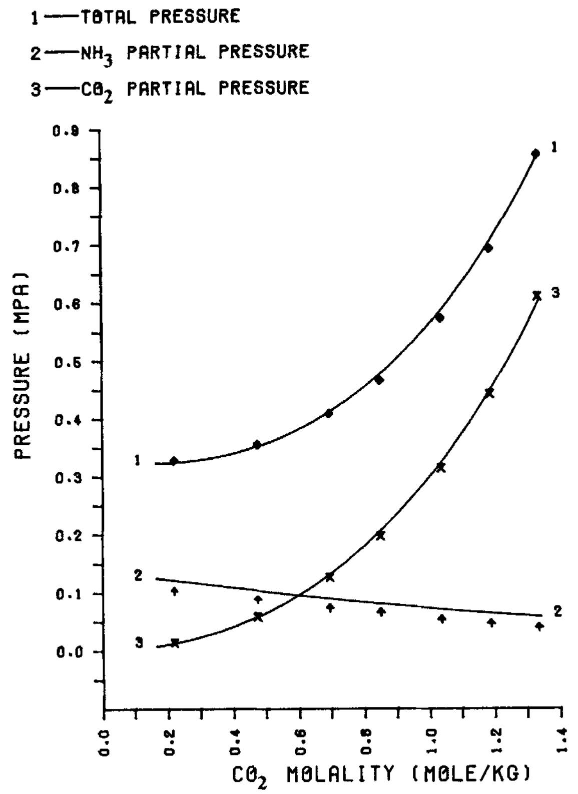

Figure 3. Predicted curves vs. experimental points: pressure vs. CO_2 molality at 393.15 K and ammonia molality 2.84.

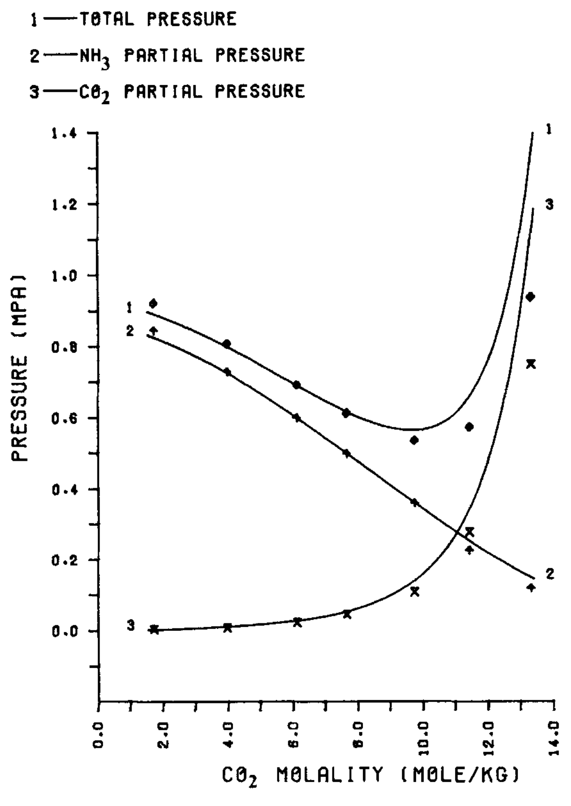

Figure 2. Predicted curves vs. experimental points at 373.15 K and ammonia molality equal to 25.9.

the comparison between calculated curves and experimental data not used in parameter estimation: both the predictions at higher concentrations, Figure 2, and those at a different temperature where the typical pressure minima are predicted at the correct value, Figure 3, are in good agreement with the experimental data.

Such a good prediction gives us confidence in the predictive capability and, therefore, in the reliability of the model. This is due to the UNIQUAC equation used to calculate the activity coefficients. In fact, such an equation is naturally predisposed to treat multicomponent systems, using interaction coefficients obtained from binary systems, because of the local composition mixing rule. Moreover, in the UNIQUAC model there are no "special" components such as water; the excess free energy is built up using water-interaction parameters. Furthermore, our assumption which treats the system as a composition of four chemical equilibrium equations instead of five (Edwards et al., 1978), simplifies the mathematical problem, but certainly it is no less powerful in simulating experimental behaviors.

Acknowledgements

The authors thank Agrimont for the helpful collaboration and for the financial support given for this work.

Notation

a_i = activity of component i
a_{ki} = interaction parameter between component k and component i
B_1, B_2, B_3, B_4 = parameters in Eq. 4

f_i = fugacity of component i
H_i = Henry's constant of component i, MPa · kg/mol
$H_i^{(P)}$ = Henry's constant of component i, at pressure P
$H_i^{(P_w^s)}$ = Henry's constant of component i, at saturation pressure
m = molality, mol/kg of solvent
P = pressure, MPa
P_w^s = saturation pressure of water at system temperature
R = gas constant, J/mol · K
T = temperature, K
V = partial molar volume, cm^3/mol
V_i^∞ = partial molar volume of molecular solute at infinite dilution
x_i = liquid mole fraction of component i
y_i = vapor mole fraction of component i

Greek letters

γ = activity coefficient
ϕ = vapor-phase fugacity coefficient

Superscripts

C = combinatorial
DH = Debye-Hückel
L = liquid phase
o = pure component
R = residual
S = saturation
V = vapor phase
∞ = infinite dilution
$*$ = unsymmetric convention
∇ = convention based on molality scale
$+$ = cation
$-$ = anion

Subscripts

i, k = component
W = water

Literature Cited

Edwards, T. J., G. Maurer, J. Newman, and J. M. Prausnitz, "Vapor-Liquid Equilibrium in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes," *AIChE J.*, **24**(6), 966 (Nov., 1978).

Göppert, U., and G. Maurer, "Vapour-Liquid Equilibria in Aqueous Solutions of Ammonia and Carbon Dioxide at Temperatures between 333 and 393 K, and Pressures to 7 MPa," *Fluid Phase Equil.*, **41**(1–2), 153 (1988).

Guillevic, J., D. Richon and H. Renon, "Vapor-Liquid Equilibrium Data for the Binary System Water-Ammonia at 403.1, 453.1, and 503.1 K up to 7.0 MPa," *J. Chem. Eng. Data*, **30**(3), 332 (1985).

Houghton, G., A. M. McLean, and P. D. Ritchie, "Compressibility, Fugacity, and Water-Solubility of Carbon Dioxide in the Region 0–36 atm and 0–100°C," *Chem. Eng. Sci.*, **6**, 132 (1957).

Maurer, G., "Phase Equilibria in Chemically Reactive Systems," *Fluid Phase Equil.*, **30**, 337 (1986).

Nakamura, R., G. J. F. Breedveld, and J. M. Prausnitz, "Thermodynamic Properties of Gas Mixtures Containing Common Polar and Nonpolar Components," *Ind. Eng. Chem. Proc. Des. Dev.*, **15**(4), 557 (1976).

Pawlikowski, E. M., J. Newman, and J. M. Prausnitz, "Phase Equilibria for Aqueous Solutions of Ammonia and Carbon Dioxide," *Ind. Eng. Chem. Proc. Des. Dev.*, **21**(4), 764 (1982).

Pitzer, K. S., "Thermodynamics of Electrolytes. I: Theoretical Basis and General Equations," *J. Phys. Chem.*, **77**(2), 268 (1973).

Sander, B., A. Fredenslund, and P. Rasmussen, "Calculation of Vapor-Liquid Equilibria in Mixed Solvent/Salt Systems Using an Extended UNIQUAC Equation," *Chem. Eng. Sci.*, **41**(5), 1171 (1986a).

———, "Calculation of Vapor-Liquid Equilibria in Nitric Acid-Water-Nitrate Salt Systems Using an Extended UNIQUAC Equation," *Chem. Eng. Sci.*, **41**(5), 1185 (1986b).

———, "Calculation of Solid-Liquid Equilibria in Aqueous Solutions of Nitrate Salts Using an Extended UNIQUAC Equation," *Chem. Eng. Sci.*, **41**(5), 1196 (1986c).

Manuscript received Mar. 7, 1988, and revision received Sept. 22, 1988.