Journal of Solution Chemistry, Vol. 25, No. 1, 1996

Equation of State for the NH_3–H_2O System

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Received May 22, 1995; revised November 13, 1995

An equation of state (EOS) for the NH_3–H_2O system has been developed. This EOS incorporates a highly accurate end-member EOS and on an empirical mixing rule. The mixing rule is based on an analogy with high order contributions to the virial expansion for mixtures. Comparison with experimental data indicates that the mixed system EOS can predict both phase equilibria and volumetric properties for this binary system with accuracy close to that of the experimental data from 50°C and 1 bar to critical temperatures and pressures.

KEY WORDS: Equation of state; chemical potential; phase equilibrium; density; H_2O; and NH_3.

1. INTRODUCTION

Mixtures of ammonia (NH_3) and water (H_2O) have been suggested as working fluids in geothermal energy conversion processes. NH_3 also occurs as one of the major gases in some geothermal reservoirs, such as Geysers Geothermal Field.[1] In order to predict the chemical behavior of NH_3 under different *PVTx* conditions, it is desirable to have a reliable equation of state (EOS). An accurate EOS should be able to predict many different properties, including chemical potentials, phase equilibria, densities, *etc.* Because of the strong polarity of both water and ammonia, the existing EOS for NH_3 have difficulties satisfying the different industrial needs. For example, the improved Peng-Robinson EOS[2] with the mixing rule proposed by Wong *et al.*[3] can predict phase equilibria but fails to predict densities.

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0095-9782/96/0100-0043$09.50/0 © 1996 Plenum Publishing Corporation

Recently, we have developed a highly accurate EOS for the binaries in the system CH_4–CO_2–H_2O.[4–5] This EOS for the binaries was generated by first finding a practical and efficient description of the end member systems (*e.g.*, CH_4). Both the liquid and gas states of the end members of the binary are described with roughly equal accuracy. A mixing rule was then developed that allows mixing of the binaries to be treated. The predictions of both densities and phase equilibria by our EOS are very nearly within experimental error for a very large range of *PVT* values. For example, the phase equilibria of the CH_4–H_2O system from 50 to 370°C and from water saturation pressure to 3500 bar was well predicted.

As a continuation of our modeling program, we extended this approach to include the NH_3–H_2O binary. First, we developed the EOS for the end-member NH_3. Using this end member EOS, together with the EOS for H_2O published previously,[4] we parameterized the mixing rule based on the existing phase equilibrium data. Because of the variation between some of the data sets, we carefully reviewed the data before parameterization.

2. THE EQUATION OF STATE

2.1. The EOS for the End-Member NH_3

In order to model complex phase behavior (such as the distribution of gasses between liquid and vapor), it is necessary to have a sufficiently flexible EOS for the end-members in the water-gas systems. We recently developed an EOS, which successfully describes both pure systems and mixtures the system CH_4–CO_2–H_2O.[4–5] The equation is also used in this study,

$$Z = 1 + \frac{BV_c}{V} + \frac{CV_c^2}{V^2} + \frac{DV_c^4}{V^4} + \frac{EV_c^5}{V^5} + \frac{FV_c^2}{V^2}\left(a_{14} + \frac{a_{15}V_c^2}{V^2}\right)\exp\left(-\frac{a_{15}V_c^2}{V^2}\right), \quad (1)$$

where

$$B = a_1 + \frac{a_2}{T_r^2} + \frac{a_3}{T_r^3},$$

$$C = a_4 + \frac{a_5}{T_r^2} + \frac{a_6}{T_r^3},$$

$$D = a_7 + \frac{a_8}{T_r^2} + \frac{a_9}{T_r^3},$$

$$E = a_{10} + \frac{a_{11}}{T_r^2} + \frac{a_{12}}{T_r^3},$$

$$F = \frac{a_{13}}{T_r^3} \quad \text{and}$$

$$V_c = \frac{RT_c}{P_c}.$$

2.2. The Binary NH_3–H_2O EOS

In our previous EOS,[5] a mixing rule based on the virial equation of state was used to extrapolate the end member behavior into the binary. A similar approach is used for the NH_3–H_2O system in this study. In such an approach, the parameters for the pure system EOS are generalized to extend across the binary. Various parameters and functional dependences are chosen on the basis of the agreement of the EOS with available liquid-vapor phase equilibria data. The mixing rule is described in Table I.

3. DATA REVIEW

Extensive *PVT* data for pure NH_3 were published before 1960. Canjar and Manning[6] summarized all the *PVT* data from Din.[7] The discrepancies between different data sets are usually less than 1.8%. The data cover the temperatures from −20 to 300°C and pressures from 1 to 1100 bar.

The earliest experimental work on the NH_3–H_2O system in the 19th century involved polar gases in water at low concentrations within the range of Henry's law. Later, the main thrust of experimental investigation was to obtain data suitable for the design of refrigeration equipment. In the first half of this century, Wucherer's work[8] was considered most reliable. He measured the bubble points and dew points up to 20 bar. However, Scatchard *et al.*[9] claimed that the smoothed data by Wucherer[8] were not precise enough to calculate free energies for refrigeration purposes. In order to check the Wucherer data and the calculation of Scatchard *et al.*, Macriss *et al.*[10] conducted a dew point study. They measured a few dew points from 15.31 to 35.91 bar and from 338.87 to 389.59 K at 0.47%, 0.93%, 1.76% and 3.59% water in ammonia by weight. Their measured vapor phase water concentrations were less than those of Wucherer[8] but higher than the calculated concentrations of Scatchard *et al.*[9] Macriss *et al.*[10] reported that the lack of precision in early ammonia-water data could lead to serious errors in the design of commercial refrigeration units.

There have been several significant sets of NH_3–H_2O data published since the Macriss *et al.*[10] compilation. Tsiklis *et al.*[11] published a phase

Table I. The Mixing Rule for Eq. (1)

$BV_c = \sum_i \sum_j x_i x_j B_{ij} V_{cij}$	$B_{ij} = (B_i^{1/3} + B_j^{1/3})/2)^3 k_{1,ij}$ $k_{1,ij} = 1$ (if $i = j$) $V_{cij} = ((V_{ci}^{1/3} + V_{cj}^{1/3})/2)^3$
$CV_c^2 = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk} V_{cijk}^2$	$C_{ijk} = ((C_i^{1/3} + C_j^{1/3} + C_k^{1/3})/3)^3 k_{2,ijk}$ $k_{2,ijk} = 1$ (if $i = j = k$) $k_{2,iij} = k_{2,jji}$ $V_{cijk} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3})/3)^3$
$DV_c^4 = \sum_i \sum_j \sum_k \sum_l \sum_m x_i x_j x_k x_l x_m$	$D_{ijklm} V_{cijklm}^4$ $D_{ijklm} = ((D_i^{1/3} + D_j^{1/3} + D_k^{1/3} + D_l^{1/3} + D_m^{1/3})/5)^3$ $V_{cijklm} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3} + V_{cl}^{1/3} + V_{cm}^{1/3})/5)^3$
$EV_c^5 = \sum_i \sum_j \sum_k \sum_l \sum_m \sum_n x_i x_j x_k x_l x_m x_n$	$E_{ijklmn} V_{cijklmn}^5$ $E_{ijklmn} = ((E_i^{1/3} + E_j^{1/3} + E_k^{1/3} + E_l^{1/3} + E_m^{1/3} + E_n^{1/3})/6)^3$ $V_{cijklmn} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3} + V_{cl}^{1/3} + V_{cm}^{1/3} + V_{cn}^{1/3})/6)^3$
$FV_c^2 = \sum_i \sum_j x_i x_j F_{ij} V_{cij}^2$	$F_{ij} = ((F_i^{1/3} + F_j^{1/3})/2)^3$ $V_{cij} = ((V_{ci}^{1/3} + V_{cj}^{1/3})/2)^3$
$\beta = \sum_i x_i \beta_i$	
$\gamma V_c^2 = \sum_i \sum_j \sum_k x_i x_j x_k \gamma_{ijk} V_{cijk}^2$	$\gamma_{ijk} = ((\gamma_i^{1/3} + \gamma_j^{1/3} + \gamma_k^{1/3})/3)^3 k_{3,ijk}$ $k_{3,ijk} = 1$ (if $i = j = k$) $k_{3,iij} = k_{3,jji}$ $V_{cijk} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3})/3)^3$

diagram from 370.15 to 623.15K, but the figure is very difficult to read. Polak and Lu[12] measured vapor-liquid equilibria in dilute solutions of ammonia in water. Pawlikowski *et al.*[13] have also reported isothermal measurements at 373.15 and 423.15K, covering a pressure range of 4 to 24.4 bar. Gillespie *et al.*[14] have measured vapor-liquid equilibria at 130, 180 and 230°C up to 70 bar. Rizvi and Heidemann[15] measured vapor-liquid equilibria from 32.6 to 345°C up to critical pressure. This data set generally agrees with the data of Gillespie *et al.*[14] very well, but disagrees with the Wucherer data by about 0.02–0.05 in mole fraction and disagrees with Guillevic *et al.*[16] by about 0.01–0.1 in mole fraction. Sassen and Kwartel[17] measured the dew points, bubble points and pressures up to critical pressure. Their data compare well with the data of Wucherer,[8] Rizvi and Heidemann[15] and Gillespie *et*

Table II. EOS Parameters for NH_3

Parameters	NH_3	Parameters	NH_3
a_1	−2.17218056D-02[a]	a_9	−9.13606670D-04
a_2	−8.57922298D-02	a_{10}	1.22931050D-05
a_3	−2.60003585D-01	a_{11}	−1.40854901D-05
a_4	2.39715057D-02	a_{12}	3.88960952D-05
a_5	−7.08038210D-02	a_{13}	4.59318106D-03
a_6	9.11596169D-02	a_{14}	3.08000000D+00
a_7	−9.01591089D-05	a_{15}	7.50000000D-02
a_8	5.59098353D-04		

[a] −0.0217218056

al.[14] Smolen *et al.*[18] reported phase equilibrium data from 20 to 140°C. This data set is consistent with the Rizvi and Heidemann[15] data on the liquid side, but differs on the vapor side by 0.02 to 0.09 in mole fraction.

In summary, extensive phase equilibrium data exist for the mixture of NH_3 and H_2O from room temperature and pressure to the critical temperature and pressure. The data reported by Wucherer,[8] Gillespie *et al.*,[14] Rizvi and Heidemann[15] and Sassen and Kwartel[17] agree with each other very well (within 0.03 in mole fraction). These data are used to evaluate the mixing rule (Table I) in this study. Although we have not found any density data for the bulk of NH_3–H_2O mixtures, our experience with the CH_4–CO_2–H_2O system[4–5] indicates that our EOS, with mixing parameters evaluated from phase equilibrium data, should accurately predict densities as well as phase equilibria as least in the binary.

4. PARAMETERIZATION AND COMPARISON WITH DATA

All the data for the pure NH_3 compiled by Canjar and Manning[6] are used to evaluate the parameters for Eq. (1) for the EOS of NH_3 (Table II). Figure 1 indicates that this EOS can predict density within an error of 1–3%. The average error over the temperature range 0 to 400°C and pressure range from 1 to 1200 bar is 0.98% in density.

The data of Rizvi and Heidemann[15] and Gillespie *et al.*[14] are used to evaluate the mixing parameters $k_{1,\,NH_3\text{-}H_2O}$, $k_{2,\,NH_3\text{-}NH_3\text{-}H_2O}$, and $k_{3,\,NH_3\text{-}NH_3\text{-}H_2O}$ as a function of temperature (Table III). It is very difficult to fit the parameters to a single temperature dependent function. Therefore, we use continuous switching fitting functions across the temperature 132°C. Figure 2 compares the predictions of our EOS with the data of Rizvi and Heidemann.[15] The error on the liquid side is in general less than 0.015 in mole fraction and less than 0.05 on the vapor side. This error is also about

Table III. The Binary Interaction Parameters of NH_3–H_2O

50–132°C	$k_1 = -5.8467319 + 3.62751754D\text{-}02\ T - 4.75183224D\text{-}05\ T^2$
	$k_2 = 1.00$
	$k_3 = 1.43703198 - 8.92041591D\text{-}04\ T - 2.83953816D\text{-}06\ T^2$
132–370°C	$k_1 = 1.96568755 - 3.14813800D\text{-}03\ T + 2.97500930D\text{-}06\ T^2$
	$k_2 = 1.22$
	$k_3 = 1.02982926 - 7.47056017D\text{-}04\ T - 1.52696340D\text{-}07\ T^2$

the experimental uncertainty. As is the usual case, it is very difficult to predict the phase equilibria around critical regions.

Although cubic EOS may be able to successfully predict phase equilibria in like species (polar-polar) systems, such as NH_3–H_2O, an EOS of this form has not been demonstrated to accurately calculate densities even in the pure systems.[2] Density data in the NH_3–H_2O mixed system are not available for comparison with our EOS predictions. However, our success in predicting densities in the pure NH_3 system (see Fig. 1) and our experience in predicting densities in the CO_2–H_2O and CH_4–H_2O mixed systems suggest that our EOS may be able to predict densities as well as phase equilibria in the mixtures.

ACKNOWLEDGMENTS

This work has been supported by funds from the Department of Energy: DE-FGO7-93ID13247 and Central Canada Potash. The suggestions by the Editor are appreciated.

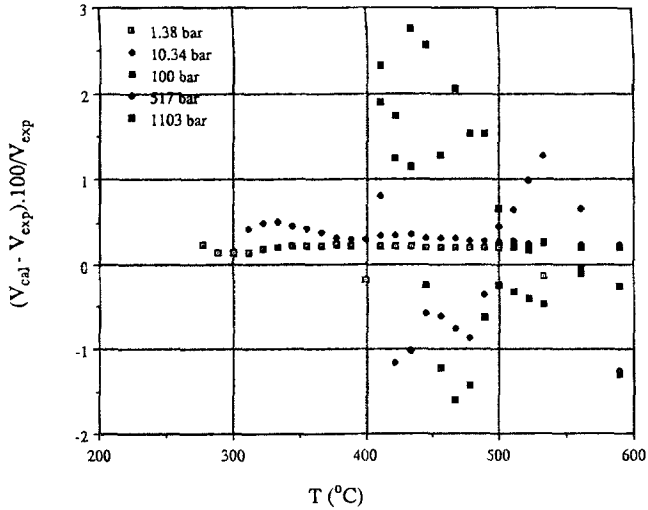

Fig. 1. Comparison of experimental density[6] of NH_3 with the predictions of our EOS as a function of temperature and pressure.

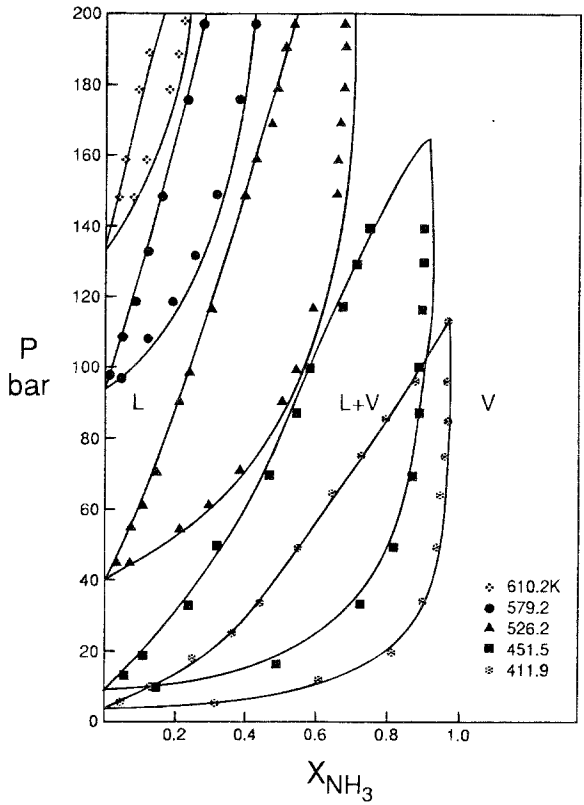

Fig. 2. Vapor-liquid phase equilibrium diagram of the system NH_3–H_2O. Comparison of the experimental data with the predictions of our EOS. The solid lines are the predictions of our EOS, and the symbols are the data by Rizvi and Heidemann.[15]

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