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Application of the Extended Corresponding States Method to the Calculation of the Ammonia–Water Mixture Thermodynamic Surface[1]

A. Nowarski[2, 3] and D. G. Friend[2, 4]

The paper presents an application of the one-fluid extended corresponding states method to the calculation of the thermodynamic surface of the ammonia–water mixture. Each pure component of the mixture is considered as a reference fluid, and to test the behavior of the model in wide ranges of temperature and pressure, the Haar–Gallagher and the Pruß–Wagner equations of state were chosen for pure ammonia and water, respectively. To avoid numerical problems during the calculation of the pure-component equivalent substance reducing ratios (or scaling factors), a method based on the mapping defined by the extended corresponding states algorithm and two-dimensional interpolation is proposed. The estimation of the binary interaction parameters was performed using the general case of the least squares method, i.e., the case when all measurements (observations) and unknowns are subject to uncertainty and are adjusted simultaneously with the constraint equations. The results show a strong temperature and composition dependence of both interaction parameters for the liquid, as well as for the vapor phase. A formulation for the binary interaction parameters as continuous functions of these variables was also derived and optimized using the structural optimization and regression analysis. The final statistical quality of the approach presented in the paper was assessed using the available data on thermophysical properties of the mixture.

KEY WORDS: *ammonia–water mixture; extended corresponding states; thermodynamic model.*

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[2] Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80303, U.S.A.

[3] Permanent address: Institute of Thermal Engineering and Air Protection, Cracow University of Technology, Warszawska 24, 31-155 Krakow, Poland.

[4] To whom correspondence should be addressed.

1. INTRODUCTION

The ammonia–water mixture is used in a variety of industrial applications. Because of its thermal properties, it is one of the most important refrigerants and has been used in absorption systems for more than 100 years. The invention of a new power cycle by Kalina [1], using the ammonia–water mixture as the working fluid, has caused a strong demand for thermophysical property data for this system, at higher values of temperature and pressure and over a wider range of concentration than was required in refrigeration applications.

This paper presents results of an application of the one-fluid extended corresponding states (ECS) method to the calculation of the ammonia–water mixture thermodynamic surface. This approach provides an alternative to the models that exist in the literature [2–6]. Because it is based on rigorous statistical mechanics, the ECS method often gives accurate predictive results, even when the thermodynamic behavior of one or more components in the mixture is poorly known.

2. ONE-FLUID EXTENDED CORRESPONDING STATES METHOD

We postulate that it is possible to map the thermodynamic surface of the ammonia–water mixture onto that of a pure, arbitrary reference fluid. This is mathematically expressed by the equation [7],

$$a_m^r(\rho_m, T_m) = a_0^r(\rho_0, T_0) \tag{1}$$

where a^r is the reduced residual Helmholtz energy, $a^r = (A - A^{\mathrm{ideal}})/RT$, R is the gas constant, T is the temperature, ρ is the density, the subscript m denotes the mixture of interest (mapped), and the subscript 0 denotes the reference fluid. Equation (1) requires relations between the densities and the temperatures of the fluids [7]:

$$T_0 = \frac{T_m}{f_m} \tag{2}$$

$$\rho_0 = \rho_m h_m \tag{3}$$

where f and h are the equivalent substance reducing ratios, or scaling factors. Assuming that the composition dependence is given by the van der Waals one-fluid mixing rules, the factors can be expressed as [7]

$$h_m = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j h_{ij} \tag{4}$$

$$h_m f_m = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j f_{ij} h_{ij} \tag{5}$$

where the cross terms are given by

$$f_{ij} = \sqrt{f_i f_j}\, k_{ij} \tag{6}$$

$$h_{ij} = \tfrac{1}{8}(h_i^{1/3} + h_j^{1/3})^3\, l_{ij} \tag{7}$$

and k_{ij} and l_{ij} are empirically evaluated binary interaction parameters, which become unity for $i = j$. To obtain values of the two *a priori* unknown factors, it is necessary to simultaneously solve Eq. (1) with an additional constraint. The most convenient constraint for computations is [7]

$$z_m^r(\rho_m, T_m) = z_0^r(\rho_0, T_0) \tag{8}$$

where z^r is a residual compressibility factor: $z^r = (p/\rho RT) - 1$, and p is the total pressure.

3. ONE-FLUID ECS AND THE AMMONIA–WATER MIXTURE

One of the most important problems in ECS is a proper choice of the reference fluid. Preliminary analysis showed that both pure components of the mixture are suitable. Calculations showed, however, that in some cases, with either ammonia or water as the reference fluid, the transformation maps from a single-phase region (liquid or vapor) to a two-phase region. This usually does not have a negative influence on the calculations, unless the resultant state point is close to the phase boundary. In this case, it can cause a non-convergence of the numerical procedure. To examine this behavior, each pure fluid was used as the reference fluid in the mixture model, and all calculations were separately performed for each case. The thermodynamic properties of the pure fluids are known with great accuracy. Very accurate equations of state are available, and in this work the Haar–Gallagher equation for ammonia [8] and a new international formulation of Pruß and Wagner for water [9] were used. The recent ammonia equation by Tillner-Roth et al. [10] was also considered, but use of this equation does not significantly modify the results of the current study.

Preliminary calculations indicated that, to achieve better accuracy in this ECS model, the binary interaction parameters have to be considered as functions of temperature and/or composition. The temperature dependence of the k_{ij} and l_{ij} parameters for this mixture was also confirmed by Smolen and co-workers [11], and this idea of temperature-dependent binary interaction parameters has been further developed in this work.

4. ESTIMATION OF THE BINARY INTERACTION PARAMETERS

The most appropriate way of obtaining values for k_{ij} and l_{ij} is to estimate them from data. Because the reference fluid was always chosen to be one of the components of the mixture, the constraint equations [which can be established using Eqs. (2)–(8)] could be written as

$$\frac{T_i}{f_i} = T_m \frac{(1-x_i)^2 + \dfrac{x_i(1-x_i)\,l_{12}}{4}(1+h_i^{1/3})^3 + x_i^2 h_i}{(1-x_i)^2 + \dfrac{x_i(1-x_i)\,k_{12} l_{12}}{4}(1+h_i^{1/3})^3 f_i^{1/2} + x_i^2 h_i f_i} \tag{9}$$

$$\rho_i h_i = \rho_m \left[(1-x_i)^2 + \frac{x_i(1-x_i)\,l_{12}}{4}(1+h_i^{1/3})^3 + x_i^2 h_i \right] \tag{10}$$

$$p_i(\rho_i, T_i)\frac{h_i}{f_i} = p_m \frac{\left[(1-x_i)^2 + \dfrac{x_i(1-x_i)\,l_{12}}{4}(1+h_i^{1/3})^3 + x_i^2 h_i \right]^2}{(1-x_i)^2 + \dfrac{x_i(1-x_i)\,k_{12} l_{12}}{4}(1+h_i^{1/3})^3 f_i^{1/2} + x_i^2 h_i f_i} \tag{11}$$

where subscript i denotes the component which is not used as the reference fluid, and $p_i(\rho_i, T_i)$ is an equation of state of the pure component i. The unknowns, k_{12}, l_{12}, T_i, and ρ_i, were estimated using the general case of the least-squares method [12], the case when all measurements are subject to uncertainty and are adjusted simultaneously with the constraint equations, Eqs. (9)–(11). In this manner, values of the binary interaction parameters were determined for each measured point, and the experimental uncertainty of every variable was explicitly considered in the regression.

4.1. Analysis of the Numerical Solution for Pure Components

It is necessary to calculate the scaling factors of the pure fluids, $h_i(\rho_i, T_i)$ and $f_i(\rho_i, T_i)$, simultaneously with the estimation of the binary interaction parameters, k_{12} and l_{12}. During the calculations, a numerical procedure may not be convergent because of the transformation of the point of interest: to the two-phase region, to the vicinity of a critical point, to outside the working area of the reference fluid equation of state, or to the low-density region. The first three problems with the transformation can usually be avoided by the proper choice of a reference fluid. In the case of ammonia–water mixtures, all of these technical problems were encountered for some state points of our preliminary analysis, independent of reference fluid. In cases when the main procedures for calculating h_i and f_i are not convergent, the solution can be found by interpolation using *a priori* prepared maps. To cover the low density region, we used a virial equation of state, truncated after the third virial coefficient. In this case, the scaling factor f_i can be calculated after solving Eq. (12) with respect to T_0, and the scaling factor h_i from Eq. (13):

$$\frac{B_0(T_0)}{B_i(T_i)}=\left(\frac{C_0(T_0)}{C_i(T_i)}\right)^{1/2} \tag{12}$$

$$h_i(\rho_i \to 0)=\frac{B_i(T_i)}{B_0(T_0)} \tag{13}$$

where B_i, C_i, B_0, and C_0 are second and third virial coefficients of the pure fluids as obtained from the full equations of state [8, 9]. Since there is no explicit density dependence in this protocol, the values of the scaling factors obtained in this way are equivalent to zero-density values. Thus, the use of two different models (the full equations of state and the truncated virial expansions) became more consistent numerically. Very good agreement with the original methods was achieved when testing the accuracy of the interpolation. Figure 1 presents a sample map of the f_{H_2O} scale factor in the vapor phase with pure ammonia as the reference fluid.

4.2. Analysis of the Numerical Solution for the Mixture

The final calculations of the binary interaction parameters were performed using data reported by Harms-Watzenberg [13] and an orthogonal distance regression algorithm developed at NIST [14]. There were 1484 points with temperatures from 243 to 498 K, pressures from 0.02 to 38 MPa, and mole fractions of ammonia from 0.1 to 0.9.

Figures 2 and 3 present the results of the estimates for k_{12} and l_{12} in the liquid and vapor phases. Both interaction parameters show a strong dependence on temperature and composition; this reflects an intrinsic shortcoming of the van der Waals one-fluid mixing and combining rules

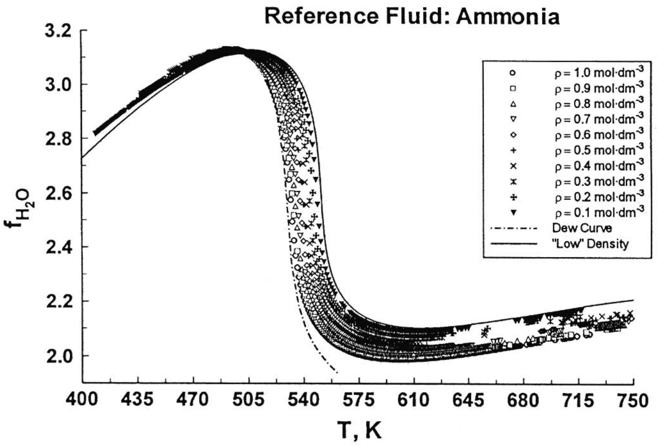

Fig. 1. The f_{H_2O} scaling factor map for the vapor phase. Reference fluid: ammonia.

[Eqs. (4)–(7)] for this system. The unusually large values for l_{12} in the vapor phase may also indicate a problem with the standard one-fluid calculations of effective molecular sizes in a system such as ammonia–water. Typical deviation plots, used to illustrate the quality of the fit, are shown in Figs. 4 (liquid phase) and 5 (vapor phase). Generally, the average

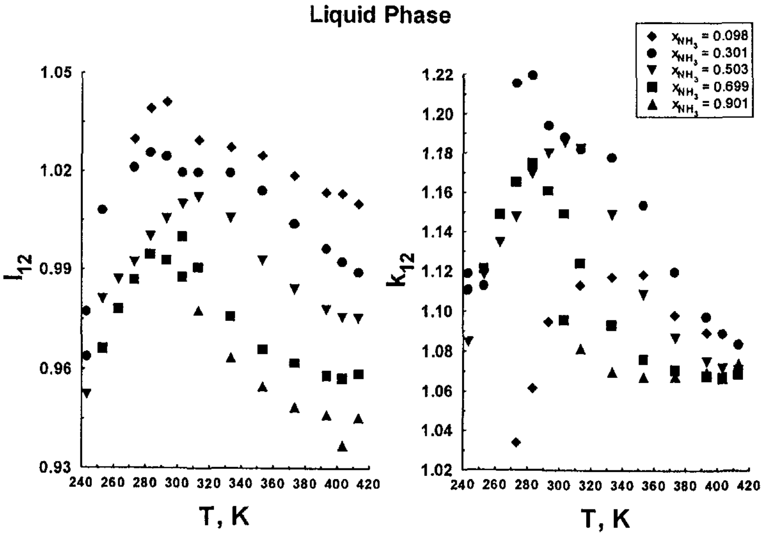

Fig. 2. Estimation of the binary interaction parameters k_{12} and l_{12} in the liquid phase; data from Ref. 13.

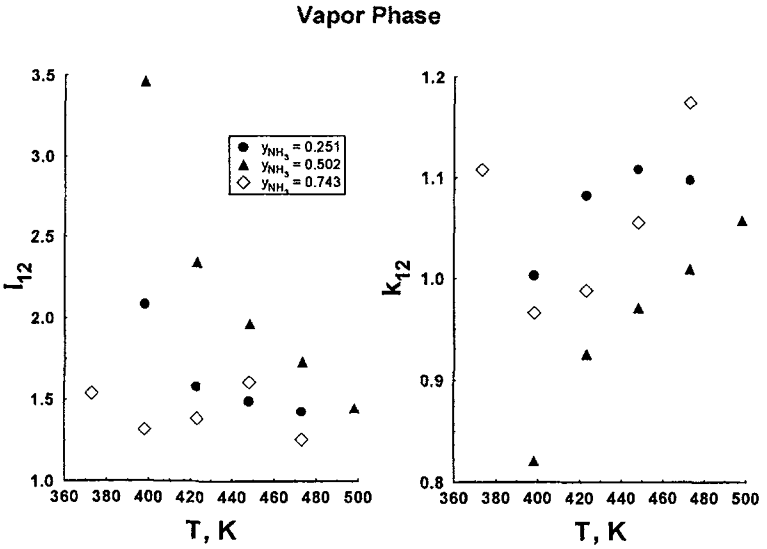

Fig. 3. Estimation of the binary interaction parameters k_{12} and l_{12} in the vapor phase; data from Ref. 13.

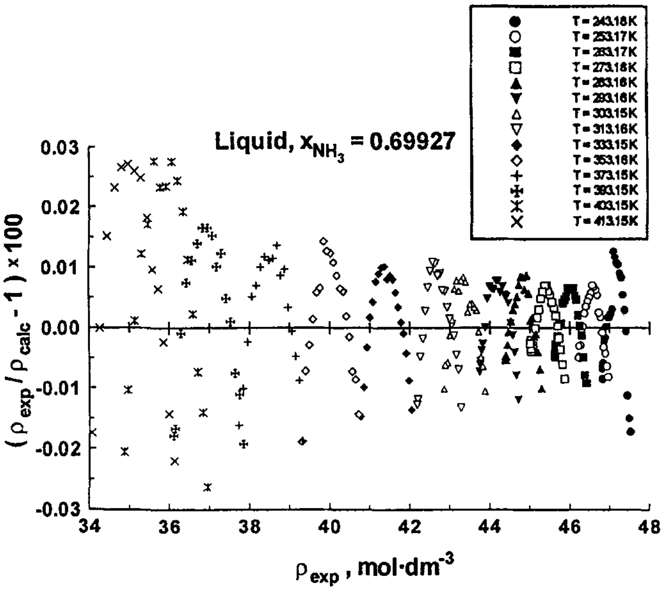

Fig. 4. Deviation plot for the density in the liquid phase; data from Ref. 13.

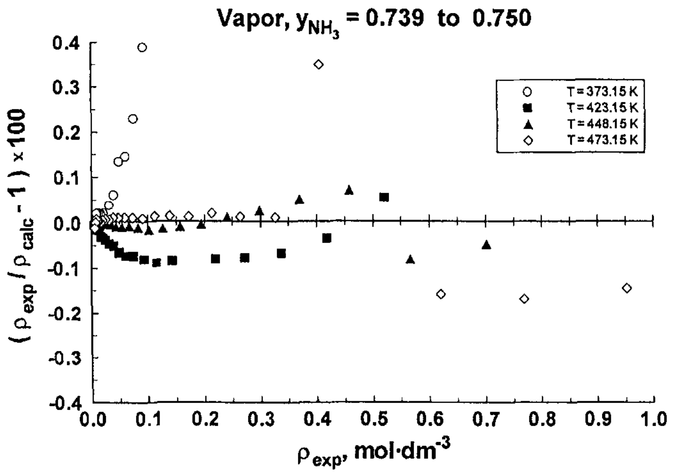

Fig. 5. Deviation plot for the density in the vapor phase; data from Ref. 13.

experimental uncertainties for densities are 0.03% for the liquid and 0.04% for the vapor phase.

The functional forms of the parameters k_{12} and l_{12} as continuous functions of temperature and composition were optimized using a structural optimization algorithm developed at the University of Hannover, Germany [15], and based on Ref. 16. The preliminary results of the optimization, valid in the range of the input data, are

$$(k_{12} \text{ or } l_{12}) = \sum_{i=1}^{N} a_i T_R^{\alpha_i} x_{NH_3}^{\gamma_i} \exp(-x_{NH_3}^{\beta_i}) \qquad (14)$$

Table I. Values of the Coefficients in Eq. (14)

Parameter	i	a_i	α_i	β_i	γ_i
k_{12}	1	1.530 532 6	0.5	1	0
	2	−0.126 101 7	3	1.5	0
	3	3.075 074 2	0	1	2
	4	−3.969 372 1	1	0.5	0.25
	5	2.341 559 9	1.5	1	0.25
l_{12}	1	−0.048 418 3	3	1	0
	2	0.161 346 5	2	1.5	0
	3	3.133 610 7	0.5	0.5	0.25
	4	−1.034 015 5	1	1	0.25

where $T_R = T^r/T$, T^r is a reference temperature ($T^r = 647.037$ K), and x_{NH_3} is the mole fraction of ammonia. We have not yet explored the effects of the form of Eq. (14) on the calculation of properties near infinite dilution. The values of the coefficients in Eq. (14) are given in Table I.

5. CONCLUSIONS

The results show that ECS can be used for strongly nonideal systems and in a wide range of temperature, pressure and composition. The use of two-dimensional interpolation and mapping made the approach more consistent numerically. The preliminary results also show that the formulation of the binary interaction parameters as functions of temperature and composition gives a significant improvement to the accuracy of density and pressure predictions. More accurate results can be achieved when reliable thermophysical property data for this system, especially near and beyond the critical region, become available.

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REFERENCES

1. A. I. Kalina, *J. Eng Gas Turbines Power* **106**:737 (1984).
2. Y. M. El-Sayed and M. Tribus, *ASME Annu. Winter Meet.* **1**:89 (1985).
3. O. M. Ibrahim and S. A. Klein, *ASHRAE Trans.* **99**:1495 (1993).
4. Y. M. Park and R. E. Sontag, *ASHRAE Trans.* **97**:150 (1991).
5. R. Tillner-Roth and D. G. Friend, *J. Phys. Chem. Ref. Data* **27**:63 (1998).
6. B. Ziegler and C. Trepp, *Int. J. Refrig.* **7**:101 (1984).
7. J. F. Ely, *Adv. Cryog. Eng.* **35**:1511 (1990).
8. L. Haar and J. S. Gallagher, *J. Phys. Chem. Ref. Data* **7**:635 (1978).
9. A. Pruß and W. Wagner, *Eine neue Fundamentalgleichung für das fluide Zustandsgebiet von Wasser für Temperaturen von der Schmelzline bis zu 1273 K bei Drücken bis zu 1000 MPa* (VDI Verlag, Düsseldorf, 1995), Vol. 320, R.6.
10. R. Tillner-Roth, F. Harms-Watzenberg, and H. D. Baehr, *Eine neue Fundamentalgleichung für Ammoniak*, Proc. 20th DKV-Tagung (Heidelberg, Germany, 1993), Vol. II, p. 167.
11. T. M. Smolen, D. B. Manley, and B. E. Poling, *J. Chem. Eng. Data* **36**:202 (1991).
12. T. Styrylska, *ZAMM Z. Angew. Math. Mech.* **71**:T393 (1986).

13. F. Harms-Watzenberg, *Messung und Korrelation der Thermodynamischen Eigenschaften von Wasser–Ammoniak-Gemischen* (VDI Verlag, Düsseldorf, 1995), Vol. 380, R.3.
14. P. T. Boggs, R. H. Byrd, J. E. Rogers, and R. B. Schnabel, *User's Reference Guide for ODRPACK Version 2.01 Software for Weighted Orthogonal Distance Regression* (NIST IR No. 4834, 1992).
15. R. Tillner-Roth, *STROPTI—Das Verfahren zur Strukturoptimierung nach Wagner*, Version 6.0 (Institut für Thermodynamik, Universität Hannover, Hannover, Germany, 1994).
16. U. Setzmann and W. Wagner, *Int. J. Thermophys.* **10**:1103 (1989).