Thermodynamic modelling of VLE behaviour at the high purification of R717 refrigerant by high-pressure batch distillation

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Abstract. The feasibility of using thermodynamic simulation models for describing the VLE behaviour of dilute ammonia-impurity solutions during high purification of R717 refrigerant by distillation is discussed. A comprehensive evaluation of different thermodynamic models (EoS-, LACT-based, combined EoS-LACT, predictive) has been done by comparing the simulation results with published experimental VLE data for ammonia-based dilute solutions in the pressure/temperature range from the boiling point of ammonia up to the critical point. The behaviour of the three important impurity groups (permanent gases, hydrocarbons, and water) in high-purity ammonia is considered in the dilute region. The studied systems are characterised by non-ideality, combine components from different chemical classes and with different polarity, contain subcritical and supercritical components, and can form associates in liquid and vapour phase. The results show that, depending on the system and the operating pressure, various modelling approaches can be successfully employed in the simulation of distillation-based separations involving VLE of non-ideal highly diluted ammonia-based mixtures. Equally important is the type of mixing rules, as well as the quality of the binary interaction parameters used in the relations. The usage of some of the predictive methods is shown to be a sensible option for a preliminary design.

1. Introduction

High-purity R717 refrigerant (ammonia, >99.994%) is generally acknowledged as being the most efficient “green” natural refrigerant having excellent thermodynamic properties and low energy requirements [1]. It has a low boiling point and is favoured because it is a highly energy efficient refrigerant which also has a minimal environmental impact, having zero ODP (Ozone Depletion Potential) and zero GWP (Global Warming Potential). Nowadays R717 refrigerant actively replaces the CFC and HCFC refrigerants according to the Montreal Protocol and the Kyoto Protocol as more environmentally safer, more energy efficient and less expensive refrigerant. Ultra-high-purity ammonia (99.9999%) is a key component of the Space Station’s thermal control systems due to its high thermal capacity and a wide range of operating temperatures [2].

The purity of the R717 refrigerant is of high importance and immediately determines the performance and reliability of the cooling system, which is critical especially for Space applications and also for industrial cooling systems. Water present in ammonia systems creates some problems,
including internal system corrosion and creation of sludge that can cause blockages in the systems. The presence of moisture impacts the vapour pressure of the system. This combined with corrosion and sludge, substantially impacts the efficiency of the system – with a notable deterioration even at levels of just 0.5%. Other impurities such as O₂, N₂ and hydrocarbons will have a similar impact, increasing the risk of corrosion, stress corrosion cracking and system performance drops.

Commercial grade ammonia (99.5%) is the largest-capacity bulk reagent in the world, readily available and inexpensive, however, the presence of water traces, oxygen-containing impurities and hydrocarbons makes it impossible to use it in high-performance cooling systems without purification [3,4].

Batch distillation in high-efficient packed columns is the most universal and widely used method for purification of specialty gases due to its high performance, versatility, the simplicity of technological scheme, and the possibility of maintaining high chemical sterility of the process. Taking into account the normal boiling point of ammonia (-33.34 °C) it is advisable to employ high-pressure distillation [5–7] to permit the condensation process at ambient temperature and avoid using energy-intensive and expensive cryogenic refrigeration systems. The increase of temperature also lowers the enthalpy of vaporisation thus promoting the further reduction of energy intensity, while the increasing pressure gives an opportunity to raise the productivity of the purification process [5].

Carrying out the distillation under higher pressure promotes the intensification of the mass transfer kinetics, however it is inevitably accompanied by a significant change in phase equilibrium [5,8]. That is why the reliable vapour-liquid equilibrium (VLE) data is required for ammonia-impurity dilute systems over a wide range of pressure and temperature to quickly and efficiently identify the best set of operating parameters for the ammonia distillation process in preliminary simulations.

The selection of an appropriate physical property method is a crucial issue in the simulation-aided process design. Inadequate thermodynamic modelling was found as one of the major causes of failure in designing distillation systems [9]. The simulation results cannot be better than the quality of the models and the associated data.

The thermodynamic properties of dilute solutions are acknowledged as being very difficult to predict and systems involving these conditions should always have the results from process simulation work validated by experimental data. Ammonia-impurity dilute solutions represent challenging complex systems, including polar species, supercritical and subcritical components of different chemical classes. Non-ideality and strong interactions solute-solvent should be accounted for [10]. In cases, when the species in the vapour phase give association, the fugacity calculation has to be modified accordingly.

The literature remains scarce regarding the modelling of VLE for ammonia-based solutions in the dilute region over a large range of pressures and temperatures. The current research aims to make a comprehensive evaluation of different thermodynamic models by comparing the simulation results with the experimental VLE data for ammonia-impurity dilute solutions in the pressure/temperature range from the boiling point of ammonia up to the critical point.

2. Materials and methods

2.1 Ammonia-based binary diluted systems

The availability of the experimental VLE data for ammonia-based binary systems [10–18] allows considering the behaviour of the three important impurity groups in high-purity ammonia: permanent gases, hydrocarbons, and water. The literature data were processed to extract the liquid/vapor distribution coefficients (K-values) in dilute region for ammonia-water [11–14], ammonia-nitrogen/hydrogen [17,18], and ammonia-acetylene [16]. Table 1 shows the concentration and temperature ranges for the experimental VLE data obtained from the literature. It is important to note that these binary systems are non-ideal, combine components from different chemical classes and with different polarity, contain subcritical and supercritical components, and can form associates in liquid
and vapour phase. Consequently, the evaluation of the ability of different thermodynamic models to describe adequately the VLE behaviour of these dilute solutions in a wide pressure/temperature range is of immediate interest.

**Table 1.** The experimental VLE data for ammonia-based binary systems.

| Impurity     | K-value at 293K | Impurity mole fraction | Temperature range, K | Reference   |
|--------------|-----------------|------------------------|----------------------|-------------|
| Water        | 450±150         | 0.0001 – 0.1150        | 293.15 – 405.71      | [11–14]     |
| Nitrogen     | 840±80          | 0.0001 – 0.0089        | 277.6 – 405.5        | [17]        |
| Hydrogen     | 1070±100        | 0.0001 – 0.0102        | 277.6 – 344.3        | [18]        |
| Acetylene    | 2.7±0.2         | 0.0280 – 0.0890        | 238.15 – 405.5       | [16]        |

2.2 Thermodynamic models and approaches

Selecting the appropriate thermodynamic model and supplying the adequate parameters is a key step in solving a simulation-aided design problem [9]. The classical methods are represented by two general groups based on the equation of state (EoS models) and liquid activity coefficient concept (LACT models).

Cubic EoS (Peng-Robinson, Soave-Redlich-Kwong) are suitable for the simulation of separation processes at higher pressure. For lower pressure, the LACT models (WILSON, UNIQUAC, NRTL) are considered to be the most accurate. The treatment can also be extended by combining the approaches based on EoS and LACT using modified EoS with appropriate mixing rules (PR with Wong-Sandler mixing rules; SRK with Michelsen-Huron-Vidal mixing rules). In the case of non-ideal mixtures, the interactions between species should be accounted for, and the quality of the binary interaction parameters (BIP) is crucial for the reliability of results. There are also predictive methods (UNIFAC, PSRK, VTPR) which make possible treating the non-ideal VLE without the knowledge of BIP fitted from experimental data.

Each of the approaches mentioned above is going to be evaluated for the ability to describe the thermodynamic properties of non-ideal ammonia-based dilute solutions to define the most efficient models for each system. The option of an ideal behaviour will also be employed for comparison purpose.

3. Results and discussion

The experimental data on VLE for ammonia-impurity systems (Table 1) demonstrates that K-values are high enough for the efficient high purification of commercial-grade ammonia by distillation. Knowledge of the phase equilibrium behaviour in a wide range of temperatures and pressures is vitally important for the rigorous simulation of the batch distillation process and optimising the operating parameters.

Water is the most critical impurity for the refrigerant-grade ammonia. The behaviour of ammonia-water solutions has been the subject of many publications [11–14]. The published data indicate that the system does not form an azeotrope and is characterised by a significant negative deviation from Raoult's law. The latter, apparently, is due to the formation of hydrates of ammonia in the liquid and vapour phases.

The experimental literature data were processed for the cases of the smallest water concentrations in ammonia to consider vapour-liquid distribution coefficients (K-values) in the dilute region. Figure 1 (left) presents a VLE analysis covering the temperature and pressure range from the normal boiling point of ammonia up to the critical point. For the convenience the K-value data is plotted in Arrhenius coordinates (natural logarithm of K-value against inverse temperature). The experimental data are presented by marks. The simulation results are obtained with Aspen Plus V9 (lines). The general experimental trend shows a gradual decrease of K-value at increasing temperature and pressure with
$\ln K$ approaching zero at the critical point due to the gradual convergence of vapour and liquid phase properties.

It may be observed that the group of cubic EoS methods (PR, RK Soave) follow relatively close the trend of the experimental data, being generally more accurate in the high-pressure region, as expected. The option of SR-Polar implemented in Aspen Plus for handling non-ideal mixtures shows good results in the area close to the critical point, but deviates from the experiment as approaching the boiling point. BWRS virial EoS demonstrates the same good agreement at high pressures with much smaller deviation in the region of low pressures.

The results of LACT-modeling for the ammonia-water dilute system (UNIQUAC, WILSON, NRTL) are in contradiction with the experimental data, especially at higher pressure. This is apparently due to the lack of binary interaction parameters required for rigorous calculations. Though the LACT models are generally able to describe very accurately the VLE of highly non-ideal mixtures, the quality of binary interaction parameters is crucial for the reliability of results. Special attention must be given to parameter regression.

Figure 1. VLE data for the ammonia-water system: (a) and (b) – comparison of simulation results (lines) and the experimental data [11–14] (dots); (c) – deviation of simulation results from the experimental data.
The computation is repeated using the models combining the approaches based on EoS and LACT. The mixing rules proposed by Wong and Sandler allow the extrapolation of BIP for LACT models from low to higher pressure. In this way, a large amount of existing experimental information can be reused. The visual inspection of PRWS and RKSWS models, which are PR and RKS EoS with the mixing rules of Wong and Sandler, shows that the accuracy of the models is quite good in the middle region. Better results are obtained with PRMHV2 and RKSMHV2 which use the mixing rules of Huron and Vidal. These models seem to provide the most accurate results among the models considered.

Figure 2. VLE data for the ammonia-nitrogen system: (a) and (b) – comparison of simulation results (lines) and the experimental data [17] (dots); (c) – deviation of simulation results from the experimental data.

For the exploratory purposes some predictive EoS and LACT methods were considered. Predictive methods make possible treating the non-ideal VLE without the knowledge of BIP fitted from the experimental data. The advantage of Predictive SRK method (PSRK) is the extension of the EoS model to mixtures of polar components without the knowledge of the experimental binary interaction coefficients [9]. The simulation results demonstrate that it is possible to make estimations using predictive methods. The predictive volume translated Peng-Robinson (VTPR) EoS, which is
recommended for application in the case whether the system contains polar, non-polar, symmetric or asymmetric, sub- or supercritical compounds, shows the same behaviour as PSRK. UNIFAC method with Dortmund modification provides significantly better prediction results for the considered system, especially for lower pressure, and generally predicts slightly better than the original UNIFAC. The modified UNIFAC model (Dortmund) introduces temperature-dependent interaction parameters [9]. The main advantage of the modified UNIFAC method is a better description of the temperature dependence and the real behaviour in the dilute region.

Figure 3. VLE data for the ammonia-hydrogen system: (a) and (b) – comparison of simulation results (lines) and the experimental data [18] (dots); (c) – deviation of simulation results from the experimental data.

The results of EoS-modeling for ammonia-nitrogen/hydrogen dilute systems demonstrate excellent accuracy (figures 2, 3). All of considered EoS models closely follow the experimental data through the entire pressure and temperature region. No clear advantage of a particular model can be seen in this type of representation. SR-Polar option demonstrates increasing deviation in the area near the boiling point. The advantage is that all components, supercritical and subcritical, are treated by EoS in the same manner.

Again, the accuracy of LACT-based methods is unsatisfactory. Since the mixture contains supercritical component (nitrogen or hydrogen) it is necessary to switch to Henry’s Gas Law method.
for vapour pressure representation of light species in the dilute region. This option improves the results of the LACT-based simulation, however, they are still far from the experimental data due to the lack of required binary interaction parameters. Simultaneous regression of Henry constant and interaction parameters of LACT is required to achieve high accuracy in gas-liquid equilibrium over a large range of pressure and temperature.

Combined EoS-LACT methods (PRWS, RKSWS, PRMHV2, RKSMHV2) do not seem to be able to provide the accurate simulation for ammonia-nitrogen/hydrogen dilute solutions either. However, the employment of predictive methods (PSRK, VTPR) allows obtaining reasonably good results. The PSRK equation is a group contribution equation-of-state which combines the SRK and UNIFAC models. This method can be used for VLE predictions over a much larger temperature and pressure range than the UNIFAC approach and is easily extended to mixtures containing supercritical compounds [9]. Additional PSRK parameters, including light gases, allows the calculation of gas/liquid equilibrium. The volume-translation modification of Peng-Robinson (VTPR) also provides a correct prediction. On the contrary, the UNIFAC method and its modifications are unable to offer satisfactory results.

Figure 4. VLE data for the ammonia-acetylene system: (a) and (b) – comparison of simulation results (lines) and the experimental data [16] (dots); (c) – deviation of simulation results from the experimental data.
Considering ammonia-acetylene dilute system, it was found that the group of cubic EoS methods do not adequately describe the VLE behaviour (figure 4). The SR-POLAR model follows the EoS curves closely. LACT-based models are closer to the experimental data, however, the Henry-constant model has missing parameters for supercritical acetylene component in ammonia solvent. WILSON-RK method describes the VLE at high pressures surprisingly well.

Combined EoS-LACT models can handle directly the supercritical components. PRMHV2 model with Michelsen-Huron-Vidal mixing rules demonstrates an excellent description of the ammonia-acetylene VLE behaviour through the entire temperature and pressure range with a slightly higher deviation at low pressure.

Predictive SRK method follows the experimental data closely with higher accuracy at lower pressure. UNIFAC prediction also provides accurate results in the area near the boiling point. As it was reported elsewhere [16] that both theoretical and experimental evidence supports the hypothesis of the bimolecular complex formation between ammonia and acetylene. To get more insight, the Hayden-O’Connell modification for UNIFAC, which may handle association, was employed. This modification seems to increase the accuracy at low pressures, but shifts deviation at high pressure. The HOC-modification employed for LACT-based models also improves the results of modelling. It is interesting to note that most of the curves have a noticeable bending near the critical point of acetylene (308.2 K).

4. Conclusion

Current paper discusses the possibility of using thermodynamic simulation models for describing the VLE behaviour of dilute ammonia-impurity solutions over a large pressure and temperature range from the normal boiling point of ammonia up to the critical point. Knowledge of the phase equilibrium behaviour in a wide range of temperatures and pressures is vitally important for the rigorous simulation of the batch distillation process and optimising the operating parameters.

The behaviour of the three important impurity groups (permanent gases, hydrocarbons, and water) in high-purity ammonia is considered in the dilute region. The experimental K-values were extracted from the literature. It is noteworthy that all binary systems studied are characterised by non-ideality, combine components from different chemical classes and with different polarity, contain subcritical and supercritical components, and can form associates in liquid and vapour phase.

The results show that, depending on the system, various modelling approaches can be successfully employed in the simulation of distillation-based separations involving VLE of non-ideal highly diluted ammonia-based mixtures. At higher pressure, cubic EoS models should always be considered. The advantage is that all components, supercritical and subcritical, are treated in the same manner. LACT-based models are designed to describe the VLE of non-ideal mixtures very accurately, however, the quality of the BIP is crucial for the reliability of results. By consequence, special attention must be given to parameter regression from the experimental data. The advantage of the combined LACT-EoS models is that they can handle directly supercritical components, as well as the gas-liquid equilibrium. Equally important is the type of mixing rules, as well as the quality of the binary interaction parameters used in the relations. Finally, the usage of some of the predictive methods is shown to be a sensible option for preliminary design. The VLE can be predicted with high accuracy without introducing new model parameters that must be fitted from experimental VLE data.

The decision strategy of selecting an appropriate thermodynamic model is generally in close agreement with the guidance presented elsewhere [9]. The future work would involve more thorough advanced analysis considering the concentration dependency of K-Values and also validating the performance of VLE thermodynamic models indirectly by simulating the purification process with chosen thermodynamic model and comparing the results with distillation column experimental data.

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List of abbreviations

ODP – Ozone Depletion Potential
GWP – Global Warming Potential
CFC – chlorofluorocarbon
HCFC – hydrochlorofluorocarbon
VLE – vapour-liquid equilibrium
EoS – equation of state
LACT – liquid activity coefficient concept
NRTL – non-random two-liquids
PR – Peng-Robinson
SRK – Soave-Redlich-Kwong
BIP – the binary interaction parameters
PSRK – Predictive SRK method
VTPR – volume-translation modification of Peng-Robinson
RK – Redlich-Kwong
SR – Schwartzentruber and Renon
BWRSM – Benedict–Webb–Rubin–Starling
PRWS – Peng-Robinson with Wong-Sandler mixing rules
RKSWS – Redlich-Kwong-Soave with Wong-Sandler mixing rules
PRMHV2 – Peng-Robinson with Michelsen-Huron-Vidal
RKSWMHV2 – Redlich-Kwong-Soave with Michelsen-Huron-Vidal
HOC – Hayden-O’Connell modification

5. References

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