

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

On thermodynamic properties of aqueous ethylamine
mixtures and modelling of excess properties

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Ethylenediamine (EDA) is a bifunctional amine used for several different purposes such as for production of the Ethylenediaminetetracetic acid (EDTA) that is used as a chelating agent in detergents but also for fungicides, bleaching activators etc. In many applications very high purity is needed and the removal of the byproduct Ethylethylenediamine (EtEDA) has proven to be difficult. Experimental data presented in this thesis showed that the relative volatility between EDA and EtEDA in the region close to pure EDA is very low. EDA and water form a maximum boiling azeotrope at atmospheric pressure and below. In both its binary mixtures with water and with EDA, EtEDA was the heaviest component at all compositions. In the ternary mixture however, EtEDA is the most volatile component in an area of composition close to the binary azeotrope. A ternary saddle point azeotrope is found at a molar fraction of 0.24 of water, 0.62 of EDA and 0.14 of EtEDA and a temperature of 392.6 K at atmospheric pressure.

Experimental data for the density of mixtures of water and EDA are also presented in this thesis. At temperatures below 300K, there is a local maximum in density in the water rich region. Thus, measurements of density cannot be used to determine the composition of EDA water mixtures in that area. The excess molar volume is negative and has unusually high amplitude. This indicates strong intermolecular forces.

In chemical engineering, reliable models for vapor-liquid equilibria (VLE) are important. There are two different approaches to VLE: with the equation of state, the one and same model is used for both phases and several different properties can be calculated with the model. It is used for calculations with non-polar compounds. For polar compounds at low pressures a Gibbs excess energy (g^E) model is used to describe the liquid phase and the vapor phase is often considered to be an ideal gas. The g^E mixing rules attempt at incorporating the information from the g^E model into the equation of state. In this thesis, the ability of some models to cross-predict excess enthalpy (h^E) and VLE was investigated. Among the g^E models included, the UNIQUAC equation was found to be the most reliable for prediction of h^E from VLE data. Flexibility has to be added to the equation by letting the binary parameters be linearly dependent on temperature. If the UNIQUAC equation is to describe both VLE and h^E reliably, both kinds of data have to be included in the estimation of the parameters. The UNIQUAC equation was incorporated in the MHV2 and Soave mixing rules for the Soave-Redlich-Kwong equation of state. For VLE temperature extrapolations it had been observed that a cancellation of errors improved the results; A lack of fit caused by an approximation done in the MHV2 mixing rule, cancelled out a common error in the temperature dependence of the UNIQUAC equation. The same phenomenon was observed for the predictions of h^E in this study.

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List of Publications

This thesis is based on the work contained in the following papers:

I. **Å.U. Burman** and H.U.K. Ström, “Calculation of vapor liquid equilibrium and excess enthalpy with the UNIQUAC equation”, *Chemical Engineering Communications*, **194**, 1029–1052. (2007)

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II. **Å.U. Burman** and H.U.K. Ström, “Excess enthalpy and vapor-liquid equilibria with the MVH2 and Soave mixing rules” *Chemical Engineering Communications*, **198**, 1435-1453. (2011)

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IV. **Å.U. Burman** and H.U.K. Ström, “Vapor Liquid Equilibrium for Mixtures of Ethylethylenediamine, Ethylenediamine and Water” *Journal of Chemical and Engineering Data*, **58**, 2, 257-263. (2014)

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1. Introduction

In modern society, we depend on chemical products such as pharmaceuticals, detergents, fuels etc. It is important that the production of these is as clean and energy efficient as possible. An energy consuming part of the production is the separation of the stream that comes from a reactor into pure products or for recirculation of reactants. Such separations are necessary to avoid emissions and to make the production environmentally sustainable. To make these processes optimal, precise knowledge of physicochemical properties such as vapor pressure, density and vapor liquid equilibrium (VLE) is necessary. Measurements are expensive and time-consuming and the number of possible combinations of compounds, concentrations, temperatures and pressures needed, quickly becomes immense. Thus, good models, that allow not only for interpolation but also for extrapolation to, for example, other temperatures and multicomponent mixtures, are essential.

1.1 Background

For VLE, two different approaches are used in engineering calculations. The $\phi\phi$ approach with an equation of state uses the same model for the liquid and the gas phase and gives a good representation of the properties of many fluids. Equations like the Soave-Redlich-Kwong (SRK, Soave, 1972) and the Peng-Robinson-Stryjek-Vera (PRSV, Stryjek and Vera, 1986) are widely used as they are straight forward to apply and as pure component parameters are published for a lot of compounds. However, they cannot model polar liquids and their mixtures very well. For such mixtures, the $\phi\gamma$ approach with a g^E -model for the liquid phase is better. The liquid phase model then originates from lattice theory. One of the drawbacks with the second approach is that a separate gas phase model is needed, which limits the use of the model to well below the critical conditions.

In an attempt to combine the two methods mentioned above, and to extract the advantages from each of them, the so called Gibbs excess free energy (g^E) mixing rules were developed during the 1990's. They aim at improving the equation of state by incorporating the compositional dependency of the g^E -models for mixtures.

Ethylenediamine (EDA; 1,2-diaminoethane. CAS 107-15-3) is a bifunctional solvent with its two amine groups. It is a strong base. In 1998 the approximated world production of EDA was $3.4 \cdot 10^8$ kg (Eller and Henkes, 2000). EDA is used directly in some special applications such as electroplating baths and as a solvent for proteins, but mostly used as a building block for other compounds. These include Ethylenediaminetetracetic acid (EDTA) that is used as a chelating agent in detergents, fungicides, bleach activators, pharmaceuticals like aminophylline and antihistamine and precursors to polymers.

In many applications, high purity of EDA is required. It has to be separated from water and EtEDA (EtEDA, CAS 110-72-5). Water and EDA form an azeotrope. That means that at a

certain composition the vapor and liquid phases have the same composition, and thus that the two compounds cannot be separated past that point through ordinary distillation. EDA is hygroscopic – it absorbs water from the air. It is also known that it is very difficult to separate EtEDA from EDA to produce highly pure EDA (Do et al. 2010).

1.2 Objectives of the study

From classical thermodynamics, it is known that excess enthalpy is closely related to phase equilibrium and specifically to its temperature dependence. The prediction of excess enthalpy will thus indicate the reliability of temperature extrapolations with the g^E mixing rules. Further, simulations of separation units are simplified if both phase equilibria and excess enthalpy can be obtained from one and the same model. The first two papers in this thesis deal with calculation and cross-prediction of excess enthalpy applying both of the two methods described.

In Paper I calculation and cross prediction of h^E with UNIQUAC as g^E -model is investigated for seven systems that exhibit different h^E behavior. Strategies for simultaneous regression for model parameters from both VLE and h^E data are discussed. Paper II contains the same kind of calculations but with the MHV2 and Soave mixing rules for the SRK equation of state and Mathias –Copeman pure component parameters, based on the UNIQUAC models from Paper I.

Paper III contains experimental density data for EDA and water. These measurements are needed both for practical purposes such as design of process equipment and in order to gain a deeper understanding of the nature of the interactions in the system.

Finally, VLE for all binary mixtures of water, EDA and EtEDA and for their ternary mixture was measured together with the vapour pressure of EtEDA. That data gives a model that can be used when deciding how to separate the mixture in the best way. The study is presented in Paper IV.

1.3 Outline of the thesis

In Chapter 2 the two approaches to VLE calculations are presented together with the development of g^E mixing rules. Excess enthalpy (h^E) is defined and the results from Paper I and II are summarized.

Chapter III gives a background to azeotropes and discusses the results of Paper IV. That paper presents the measurements of VLE for the binary mixtures of water, EDA and EtEDA at 20 kPa, 50 kPa and atmospheric pressure, and for the ternary at atmospheric pressure, as well as

the vapor pressure of EtEDA. Parameters for the UNIQUAC equation were fitted to all data available.

Chapter 4 discusses the results of the measurement of density for mixtures of EDA and water at 2 MPa presented in Paper III. An introduction of excess molar volume is also given there as well as a discussion on the different interpretations of the V^E behavior of EDA and water presented in literature.

In Chapter 5, MHV2 calculations for the data from Paper IV are presented as well as cross prediction of h^E with the UNIQUAC equation. Predictions of the excess volume (V^E) with the MHV2 model are compared with results from Paper III.

The conclusions are found in Chapter 6 and suggestions for future work in Chapter 7.

In the appendix, the prediction of vapor pressure for EDA, EtEDA, methylethylenediamine and monoethanolamine with corresponding state methods are compared with experimental data.

2. Engineering models for VLE and h^E

There are two different approaches to VLE calculations for non-electrolytes: the $\phi\gamma$ and the $\phi\phi$ approaches. With the $\phi\gamma$ approach, also called mixed model, the gas phase is described by an equation of state, typically ideal gas is assumed, and the liquid phase by a g^E or activity factor, γ , model. This approach is often applied to calculations for polar mixtures and polymer solutions at moderate pressure. When the $\phi\phi$ approach is used, both phases are described by one model: an equation of state. This method may be applied to a variety of pressures, but performs best for non-polar mixtures of hydrocarbons. Calculations for mixtures require mixing rules and combining rules. The g^E mixing rules are an attempt to incorporate the information from a g^E model into a cubic equation of state.

The two first papers in this dissertation are concerned with the modelling of VLE and excess enthalpy, h^E , with these two approaches. Excess enthalpy, or heat of mixing, is defined as the heat absorbed when a mixture is produced from the pure constituents at constant temperature and pressure. Exothermic mixtures produce heat on mixing and thus have a negative h^E . Endothermic mixtures absorb heat and have a positive h^E . The behavior can be very complicated, with h^E changing sign for different compositions and temperatures. The Gibbs excess free energy is:

$$g^E = h^E - Ts^E \quad (2.1)$$

Strange behavior in h^E and s^E (excess entropy) is often cancelled out, making g^E a simpler function.

The excess enthalpy is related to the Gibbs excess energy through the Gibbs-Helmholtz equation:

$$h^E = -RT^2 \frac{\partial}{\partial T} \left(\frac{g^E}{RT} \right) \quad (2.2)$$

As seen, h^E is related to the temperature dependence of g^E and thus to the VLE model. Paper I is concerned with this modeling using a g^E model and Paper II with an equation of state model.

2.1 Gibbs excess free energy models

Vapor-liquid equilibrium calculations are based on that the chemical potential for a component is equal in the both phases at equilibrium. The temperature and pressure of the two phases are also equal. This may also be expressed as equality in fugacities (see for example Prausnitz et al. 1986). The typical assumptions made when applying the $\phi\gamma$ approach gives:

$$\phi_i^V y_i P = \gamma_i x_i P_i^\circ \quad (2.3)$$

This is written according to the symmetrical convention ($\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$ for all components) and the standard state is pure saturated liquid at system temperature. The activity coefficient (or activity factor), γ_i , is a partial molar excess Gibbs free energy, defined by:

$$RT \ln(\gamma_i) = \left(\frac{\partial (n_{Tot} g^E)}{\partial n_i} \right)_{T, P, n_j \neq i} \quad (2.4)$$

The Gibbs excess free energy, g^E , may be described by different kinds of models. As it is an excess property, and zero for pure components, it can be described by mathematical expressions such as the Margule equation (Margule, 1895) and expansions such as the Redlich-Kister equation (Redlich and Kister, 1948). The van Laar equation and its expansions (the Wohl expansion (Wohl, 1946) etc.) are semi-theoretical expressions partially derived from the van der Waals equation of state. The most successful g^E models are the local composition models: the Wilson (Wilson, 1964), the Non-Random-Two-Liquid (NRTL) (Renon and Prausnitz, 1968) and the UNiversal QUAsi-Chemical (UNIQUAC) (Abrams and Prausnitz, 1975).

Wilson (1964) started off from the Flory-Huggins equation (Flory, 1942 and Huggins, 1942) that is derived from lattice theory. Since short-range interactions and ordering on the micro level are important for liquid properties, he substituted the bulk compositions for local compositions. These were then related to bulk compositions through Boltzmann factors.

In studies using molecular simulation it has been found that the impact of intermolecular forces is overestimated for the local composition approach. Jonsdottir (1995) succeeded in determining UNIQUAC parameters from molecular mechanics.

When no experimental data is available, the activity coefficient may be estimated using group contribution methods, such as the ASOG (Kojima and Tochigi, 1979) or UNIFAC (Fredenslund et al. 1977). Fredenslund and Sørensen (1994) give a review of those methods.

The UNIQUAC equation is described in Paper I. There, cross prediction of h^E from VLE for the three local composition methods were compared in an introductory study. With parameters from the DECHEMA series (1979-1997) without temperature dependence, the UNIQUAC equation performed best. Still, temperature dependence was necessary to introduce more flexibility in the models: both in order to model skewed curves and curves with high amplitude in the enthalpy. Temperature dependent parameters fitted to VLE data often produced bad predictions of h^E . The conclusion was that the parameters should be fitted to VLE and h^E data simultaneously when that is possible. In the main study in Paper I, different expressions for the temperature dependency were compared. A linear temperature dependency was found to be the most numerically stable and to give a reasonable fit to the data. Simultaneous regression of h^E and VLE data made the parameter estimation procedure less dependent on the initial estimates for the parameters. Cross-prediction of VLE from parameters fitted to h^E for two temperature levels was not quantitative. The Anderson modification of the UNIQUAC equation performs slightly better than the original version. Cross-prediction of h^E from VLE data typically resulted in h^E curves that were too simple and too low in amplitude. With parameters fitted simultaneously to h^E and VLE data, both kinds of data could be calculated with good accuracy. However, the precision was lower than when VLE data was calculated from a model fitted only to VLE data and h^E data calculated from a model fitted only to h^E data. The problem with cross-prediction is not merely about the models, but also about the information contained in the different types of data.

2.2 Cubic equations of state

The cubic equations of state are volumetric equations of state, i.e. they are expressions for the pressure with temperature, volume and composition as independent variables: $P(T, v, n_i)$. These independent variables are the canonical variables for the Helmholtz free energy, $A(T, v, n_i)$, that may be seen as the generating function for the volumetric equations of state. The rules set by classical thermodynamics on such models are reviewed by Mollerup (1993). The ideal gas law, the simplest volumetric equation of state, may be obtained from statistical thermodynamics assuming that the molecules in a fluid have no extension and no interaction with each other. Virial equations of state are series expansions with the ideal gas law term as the first term.

The first cubic equation of state was developed by van der Waals (1873). He introduced the co-volume, b , to account for the volume occupied by the molecules. Since the pressure in a real gas is reduced by attractive forces between molecules, the term $-a/V^2$ is added to the expression. The van der Waals equation of state is:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (2.5)$$

Given the temperature and the pressure, there are three volumes satisfying Equation 2.5: hence the name cubic. The smallest root is the liquid volume and the greatest is the vapor phase volume. The a and b parameters may be found using the conditions for the critical point:

$$\left(\frac{\partial P}{\partial V} \right)_T \Big|_c = 0 \quad \left(\frac{\partial^2 P}{\partial V^2} \right)_T \Big|_c = 0 \quad (2.6)$$

The original van der Waals equation of state produces only a qualitative description of the fluid; the critical compressibility is wrong and the predicted vapor pressures inaccurate.

Several modifications of the attractive term in Equation 2.5 have been proposed; some authors changed the volume and temperature dependencies (Redlich and Kwong, 1949, and Peng and Robinson, 1976) and others introduced additional parameters (for example Schmidt and Wenzel, 1980, Heyen, 1980, and Patel and Teja, 1982). Volume translations ($V \rightarrow V+c$ and $b \rightarrow b+c$) that improve the predictions of liquid densities have been presented (Peneloux et al., 1982, Chou and Prausnitz, 1989).

The Soave-Redlich-Kwong (Soave, 1972), SRK, equation of state is commonly used in engineering calculations. It is:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (2.7)$$

The pure component parameters are calculated as:

$$a_{ii} = 0.4286 \frac{(RT_{ci})^2}{P_{ci}} (f(T_{ri}))^2 \quad (2.8)$$

$$b_{ii} = 0.08664 \frac{RT_{ci}}{P_{ci}} \quad (2.9)$$

Soave proposed a predictive expression $f(T_{ri})$ using the acentric factor. However, a better fit to vapor pressure of polar compounds may be achieved by using one of the empirical equations proposed. A commonly used expression is the Mathias-Copeman equation (Mathias and Copeman, 1983):

$$f(T_{ri}) = \left(1 + c_1(1 - T_{ri}^{1/2}) + c_2(1 - T_{ri}^{1/2})^2 + c_3(1 - T_{ri}^{1/2})^3 \right) \quad (2.10)$$

The SRK and PR equations of state are widely used in engineering calculations. They are simple to apply but they fail for example when liquid densities are calculated and they do not account for hydrogen bonding in an explicit way (Avlund, 2011).

Lately, different developments for the SRK equation of state have been made: The CPA (Cubic Plus Association) equation of state (Kontogeorgis et al. 1996) combines the Helmholtz expression for the SRK equation of state with the association term from the SAFT (Statistical associating fluid theory, Chapman et al. 1989). This introduces two new pure component parameters: an associating energy parameter and an associating volume parameter. An association scheme for the mixture has to be chosen as well. According to Avlund (2011) the model is promising but problems regarding how to estimate parameters and choose association scheme are still to be solved.

Lucia, 2009, presented the Gibbs-Helmholtz constrained equation of state, based on the SRK equation of state, for reservoir fluids at high pressures. It uses theoretical parameters; b is set to the solid molar volume and a is computed through Monte Carlo simulation. The author claims that he has a simplified way of performing the Monte Carlo simulations. The approach will need to be adapted for lower pressures.

2.2.1 Conventional mixing rules

When cubic equations of state are applied to mixtures, it is assumed that the same functional expression may be applied to mixtures as to pure components. This is the so called one-fluid theory. New values for the a and b parameters of the mixture are calculated using mixing rules. The van der Waals one-fluid mixing rules (also called the conventional or the quadratic mixing rules) are the most commonly used for engineering calculations. The rules for the a_{ij} and b_{ij} parameters are called combining rules.

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad a_{ij} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) \quad (2.11-12)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad b_{ij} = \frac{b_{ii} + b_{jj}}{2} (1 - l_{ij}) \quad (2.13-14)$$

The number of interaction parameters used varies. Often only one parameter $k_{ij}=k_{ji}$ is estimated and l_{ij} is set to zero, but attempts have been made to ameliorate the mixing rule by adding temperature dependence to both the k_{ij} and l_{ij} parameters, giving a total of four estimated parameters (Knudsen et al. 1993). When l_{ij} is zero, the resulting mixing rule for the b parameter of the mixture, is linear.

These mixing and combining rules can be derived from the Lorentz-Berthelot mixing rules for the size and attractive energy parameters in the Lennard-Jones potentials, using the mean field

approximation (Nordholm, 1995). According to Nordholm, $(1-k_{ij})$ is often smaller than one. His interpretation of this is that when two different kinds of molecules are mixed, the energy levels are no longer perfectly matched, and the resonance enhancement in a pure fluid is lost. The van der Waals one-fluid mixing rules are consistent with the requirement from statistical mechanics that the second virial coefficient be quadratic in composition and the third cubic (Sandler et al. 1994).

For modeling of VLE behavior of petroleum fluids and mixtures that can be described by regular solution theory, the van der Waals mixing rules have proven excellent, but they are not reliable for polar mixtures. They are not successful for mixtures that differ too much in molecular size and in critical temperature (Sandler et al. 1994). Sandler et al. (1994) analyzed the expression for Gibbs free energy obtained from a cubic equation of state with the van der Waals mixing rules and found that it consists of three parts: one Flory free volume term (similar to the UNIQUAC combinatorial term), one term similar to g^E of regular solution theory and one term similar to a term from augmented regular solution theory.

In Paper II the h^E predictions with the van der Waals mixing rule were included as a reference. When no binary parameter or one binary parameter was used, the model could only produce symmetrical h^E curves. Over all, the predictions of h^E with the van der Waals mixing rules was improved on the introduction of a binary parameter estimated from VLE data, but for some systems it deteriorated.

The $\phi\phi$ approach has several advantages to the $\phi\gamma$ approach:

- Expressions for thermodynamic properties can be derived from the equation of state to allow for calculation of enthalpies, entropies and densities.
- It is possible to calculate properties of mixtures at high pressure and close to the critical point with an equation of state. Since the $\phi\gamma$ approach uses one model for the liquid phase and another for the gas, it cannot model continuity at the critical point (Knudsen et al. 1993). Further, the local composition g^E models are developed to handle the moderate excess properties of a sub-critical compounds and thus cannot handle the much greater excess properties in a mixture in which one component is supercritical (Lermite and Vidal, 1988).
- Cubic equations of state are applicable in a wide range of pressures and temperatures with only a few parameters (Wong and Sandler, 1992).
- The g^E models need defined standard states. When equations of state are used there is no need to introduce hypothetical phase conditions (Wong and Sandler, 1992).

It would thus be desirable to find a way of applying the equation of state approach to polar mixtures. Mollerup (1981) showed that that is necessary to change the compositional derivatives of the model, and that this has to be done by changing the mixing rules.

2.2.2 The Gibbs excess free energy mixing rules – first attempts

The Gibbs excess free energy mixing rules were developed as an attempt to make it possible to handle mixtures with polar compounds and high-pressure (even supercritical) VLE with one and the same cubic equation of state model. The hope was that successful incorporation of an already parameterized g^E model into an equation of state could enable

the use of low pressure VLE data to the prediction of high pressure VLE. Such a model could also be made predictive by using some group-contribution method.

Although the idea of combining two different theories might appear strange, it is actually the tying together of two lines of development that originally departed from the same assumptions; as pointed out by Heidemann (1996), the van Laar theory of liquid solutions (the first g^E model with a theoretical background) is based upon the van der Waals equation of state and the van der Waals mixing rules.

The first g^E mixing rule was suggested by Huron and Vidal (1979). They equated the expression for g^E obtained from an equation of state at infinite pressure with that from a g^E model, obtaining a new mixing rule for the a parameter of the mixture. In order for g^E from the equation of state at infinite pressure to be finite, they had to assume zero excess volume and a linear mixing rule for the b parameter. Soave et al. (1994) show that the parameters can be estimated from data of the activity coefficient at infinite dilution, γ_∞ , using only the residual part of UNIFAC as g^E model. A major drawback with the HV mixing rule is that due to the match at infinite pressure, low pressure g^E model parameters cannot be used (Mollerup, 1993). Wong and Sandler (1992) criticize the model because it does not produce a quadratic composition dependency for the second virial coefficient. They also show that when A^E (the Helmholtz excess free energy) rather than g^E is used for the match, the constraint on the mixing rule for the b parameter is relieved.

Aiming towards an equation of state model that could use the UNIFAC equation, Gupte et al. (1986) and Gani et al. (1989), developed the UNIWAALS model for which the match of g^E 's is made at system pressure. The a parameter for the mixture is a function of the pressure that can be written as the volume derivative of the Helmholtz residual energy. Using this approach, the pressure and the volume are related to each other through a differential equation, which increases the computational hassle dramatically (Mollerup, 1993).

2.2.3 Implicit zero-pressure reference mixing rules

If the g^E 's are equated at zero pressure, the problem with the differential equation for the pressure is avoided. Since the liquid is rather incompressible, the error introduced is only of the order PV^E/RT (Heidemann, 1996).

With the dimensionless parameters $\alpha = a/bRT$ and $u=V/b$, the SRK equation of state can be written as:

$$P = \frac{1}{u-1} - \frac{\alpha}{u(u+1)} \quad (2.16)$$

Introducing:

$$q(\alpha, u) = -1 - \ln(u-1) - \alpha \ln\left(\frac{u+1}{u}\right) \quad (2.17)$$

A^E expressed in dimensionless variables may be written as:

$$\frac{A^E}{RT} = q(\alpha, u) - \sum_i z_i q(\alpha_{ii}, u_{ii}) - \sum_i z_i \ln\left(\frac{b}{b_{ii}}\right) \quad (2.18)$$

A relation between u and α may be obtained by setting the pressure to zero in the equation of state (Equation 2.15), solving for u and selecting the smallest root (i.e. the liquid root):

$$u = \frac{1}{2} \left(1 - \alpha - \sqrt{1 - 6\alpha + \alpha^2} \right) \quad (2.19)$$

The procedure, resulting in an implicit mixing rule for the a parameter of the mixture, was suggested by Mollerup (1986) and implemented by Michelsen (1990a) and, independently, by Heidemann and Kokal (1990).

As may be seen from Equation (2.19), it is not possible to find a liquid root to the equation of state at zero pressure for $\alpha < 3 + 2\sqrt{2}$ corresponding to $T_r \approx 0.8$. Procedures for extrapolation are proposed by Michelsen (1990 a,b) and by Heidemann and Kokal (1990). A linear mixing rule for the b parameter of the mixture is used in most studies. Michelsen (1996) claims that the match is close to exact regardless of the mixing rule that is chosen for the b parameter. Differences between g^E s from the equation of state and from the g^E model can arise from the true pressure being far from zero, from differences in vapor pressure and vapor behavior predicted with the equation of state and g^E model, and, at high temperatures, from inaccuracies in the extrapolation procedure (Heidemann, 1996).

2.2.4 Explicit zero-pressure reference mixing rules

Several simplifications of the implicit mixing rules that give explicit mixing rules have been proposed. Some of these were derived using other assumptions than the zero pressure approach, but results in the same type of expressions. Since α and u are related, $q(\alpha, u)$, can be thought of as depending only on α . Michelsen (1990b) uses a linear approximation for $q(\alpha)$: $q(\alpha) = q_0 + q_1\alpha$. The approximation equation was fitted to $q(\alpha)$ for $10 < \alpha < 13$ and the recommended value for q_1 is -0.593. This gives:

$$\alpha = \sum_i z_i \alpha_{ii} + \frac{1}{q_1} \left(\frac{g^E}{RT} + \sum_i z_i \ln\left(\frac{b}{b_{ii}}\right) \right) \quad (2.20)$$

Since the resulting expression was similar to the HVs, Dahl and Michelsen (1990) chose to call it the modified Huron Vidal first order mixing rule (MHV1). With a second order polynomial expression $q(\alpha) = q_0 + q_1\alpha + q_2\alpha^2$, where $q_1 = 0.478$ and $q_2 = 0.0047$, the MHV2 mixing rule is obtained:

$$q_1 \left(\alpha - \sum_i z_i \alpha_{ii} \right) + q_2 \left(\alpha^2 - \sum_i z_i \alpha_{ii}^2 \right) = \frac{g^E}{RT} + \sum_i z_i \ln\left(\frac{b}{b_{ii}}\right) \quad (2.21)$$

Soave (1992) proposed a new $q(\alpha)$ expression, derived to be asymptotically correct when the temperature approaches infinity:

$$q(\alpha) = 3.365 - \frac{\left(\alpha \ln(2) + \sqrt{(\alpha \ln(2))^2 + 69} \right)}{2} \quad (2.22)$$

When a linear mixing rule for the b parameter is applied, the zero-pressure mixing rules do not produce the required quadratic composition dependency for the second virial coefficient.

This can however be obtained by choosing another mixing rule for b as shown by Tochigi et al. (1994). They applied procedure similar to the one proposed by Wong and Sandler (1992) to the MHV1 mixing rule and found that their model performed equally well as the MHV1 in VLE calculations.

Holderbaum and Gmehling (1991) developed a mixing rule model called the predictive Soave-Redlich-Kwong (PSRK) model. Instead of matching g^E at zero pressure, they assumed constant packing fraction ($b/V=b_i/V_i=1/u$). Non-polar compounds typically have u values from 1.2 to 1.3 at 1 atm for the SRK equation of state. For polar compounds, u is lower; water has $u=0.896$. Fitting the PSRK model to VLE data, with the UNIFAC equation as g^E model, Holderbaum and Gmehling (1991) found that the best choice of u was 1.1. The PSRK model has the same expression for the a parameter of the mixture as the MHV1, but the q_1 value is -0.6466 . The MHV1 q_1 value corresponds to a u value of 1.235 (Fisher and Gmehling, 1996). Orbey and Sandler (1995) derived a similar model, OSHV (Orbey-Sandler-Huron-Vidal), but use $u=1.0$ (corresponding to $q_1=\ln(0.5)=-0.693$).

As discussed in Paper II, the PSRK and MHV1 have been shown to perform better in temperature extrapolations than the MHV2 in many cases (Fischer and Gmehling, 1996). This is explained as a cancellation of errors. There is a discrepancy between the $q(\alpha)$ computed by the mixing rule and the true $q(\alpha)$ due to the approximating equation used to make the mixing rule explicit. This discrepancy cancels out a common error in the temperature dependence of the g^E model (Michelsen, 1996). The same phenomenon was observed for the crossprediction of h^E from VLE data in Paper II: MHV2 with DECHEMA parameters performed better than the UNIQUAC model used alone with the same parameters. It also performed better than the Soave mixing rule; the discrepancy between the $q(\alpha)$'s is larger for the MHV2 mixing rule than for that by Soave. This could be noted especially for systems containing water at 25°C as $\alpha>18$ for water there and the MHV2 $q(\alpha)$ was fitted to $\alpha<18$.

In Paper II two g^E mixing rules, MHV2 and Soave, are compared for both calculation of VLE and h^E data and for cross-prediction. The g^E model applied was the UNIQUAC model from Paper I. None of the models could obtain good VLE with parameters fitted only to h^E data. The parameters for the temperature dependence of the pure component a parameter were also shown to influence the calculated h^E , as could be expected.

Other aspects on the performance of the MHV2 mixing rule are discussed in Paper II.

3. Vapour-liquid equilibrium for water, ethylenediamine and ethylethylenediamine

Vapour-liquid equilibrium (VLE) data are essential when planning for how and if a mixture is to be separated through distillation. Furthermore, the data give information on the nature of the molecular interactions in the mixture. The binary mixture of ethylenediamine (EDA) and water is known to have an azeotrope (Wilson, 1935; Rivenq, 1963; Hirata et al. 1969 and Schmelzer and Quitzsch, 1973). Ethylethylenediamine (EtEDA) is produced as a by-product in the reaction when EDA is produced from ethylene oxide and is known to be difficult to separate from EDA through distillation (Do et al. 2010, DE ANDRA PATENTEN)

Paper IV contains the results from measurement series of the vapor pressure for EtEDA and of vapour liquid equilibrium for the binary mixtures of water and EDA, water and EtEDA, and EDA and EtEDA, and for the ternary mixture. The method for the measurement and the determination of compositions are presented in the paper. Parameters for the Antoine equation for EtEDA and binary interaction parameters for the UNIQUAC equation are estimated. These are applied to calculations for the ternary mixture.

In this chapter, the concept of azeotropy is introduced and the azeotropes in the mixtures of water, EDA and EtEDA are discussed.

3.1 Azeotropy

An azeotropic point is a point for a mixture, where the concentrations of the components in the vapor phase and liquid phase are equal. Thus, it is not possible to separate that mixture by ordinary distillation. Azeotropes are common; about half of the systems in the DECHEMA series have an azeotrope (Hilmen, 2000). Most of these are found in systems that have a single liquid phase. They are called homoazeotropes. An azeotrope occurs when the total pressure curve vs. composition at a specified temperature has a tangent that is horizontal, see figure 3.1.

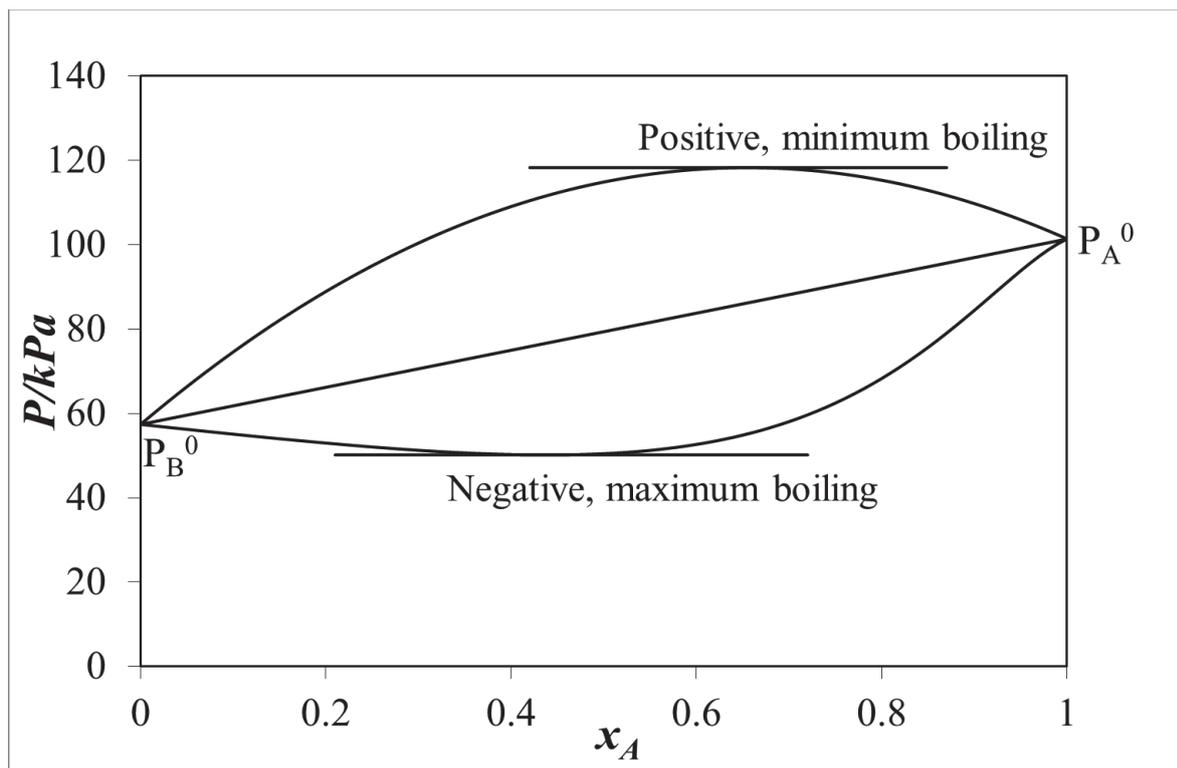


Figure 3.1 In a binary mixture, an azeotrope occurs when the total pressure curve has a tangent that is horizontal.

The straight line in Figure 4.1 from P_A° to P_B° represents Raoult's law. In a mixture that obeys Raoult's law, an ideal mixture, the interaction forces between A-A, A-B, and B-B molecules are equal. One obvious case of azeotropy is thus for an ideal mixture when $P_A^\circ = P_B^\circ$. This is called a Bancroft point and generally occurs when the vapor pressure curves of two compounds cross each other.

Azeotropy also occurs in real mixtures when they deviate enough from Raoult's law to cause the tangent of the total pressure curve to be horizontal. If the deviation is positive, that is for mixtures in which interaction between like molecules are preferred, A-A and B-B instead of A-B, a positive, minimum boiling azeotrope is formed. More than 90% of all known azeotropes are positive (Hilmen, 2000). Mixtures in which the A-B interaction forces are greater than the A-A and B-B interaction forces, exhibit negative deviation from Raoult's law. If the deviation is great enough a negative or maximum boiling azeotrope is formed. Generally, when the boiling points of two compounds are close to each other, they are more likely to form an azeotrope, as the degree of unideality required for the tangent to be horizontal, is smaller. According to Perry and Chilton (1977), homoazeotropes between components with a difference in boiling point greater than 30 K, are very rare. When a system is nearly azeotropic in a pure component edge, it is said to have a tangential pinch (Hilmen, 2000).

A few double azeotropes are reported in the literature. One of these is benzene and hexafluorobenzene at 120kPa. For that system the boiling points of the pure components are close to each other, 358.7K and 358.85K, and the azeotropes are at 358.86K and 357.74K (Aucejo, et al. 1996). Olson (2001) found that methylethylenediamine and water has a maximum-boiling azeotrope below 32.7 kPa and possibly double azeotropes between 32.7 kPa and 46.7 kPa. The results may be an artifact caused by impurities in the methylethylenediamine according to Olson.

In a ternary or multicomponent mixture, not only minimum and maximum boiling azeotropes may occur, but saddle points are also possible. Only some combinations of binary and ternary azeotropes have been observed and Hilmen, 2000, has investigated how common different combinations are in published data.

3.2 Azeotropes the mixture of water, EDA and EtEDA

As expected, a binary azeotrope was found for the binary mixture of water and EDA in the experimental data presented in Paper IV. The azeotrope is maximum boiling and thus the deviation from Raoult's law is negative. There even seems to be a minimum in the activity coefficient for water.

For EtEDA and water, no binary azeotrope was found. This is to be expected as the difference in normal boiling point is 29K. The deviation from Raoult's law is negative for this system as well and it is possible that the activity factor for water passes through a minimum see Figure 4.2. More data is needed to confirm this though. If the model in Paper IV for EtEDA and water is extrapolated, an azeotrope enters at the pure water end at a pressure of 2 kPa. This extrapolation is however not reliable as it is far from the temperature range of both the vapor pressure data for EtEDA and the UNIQUAC parameters.

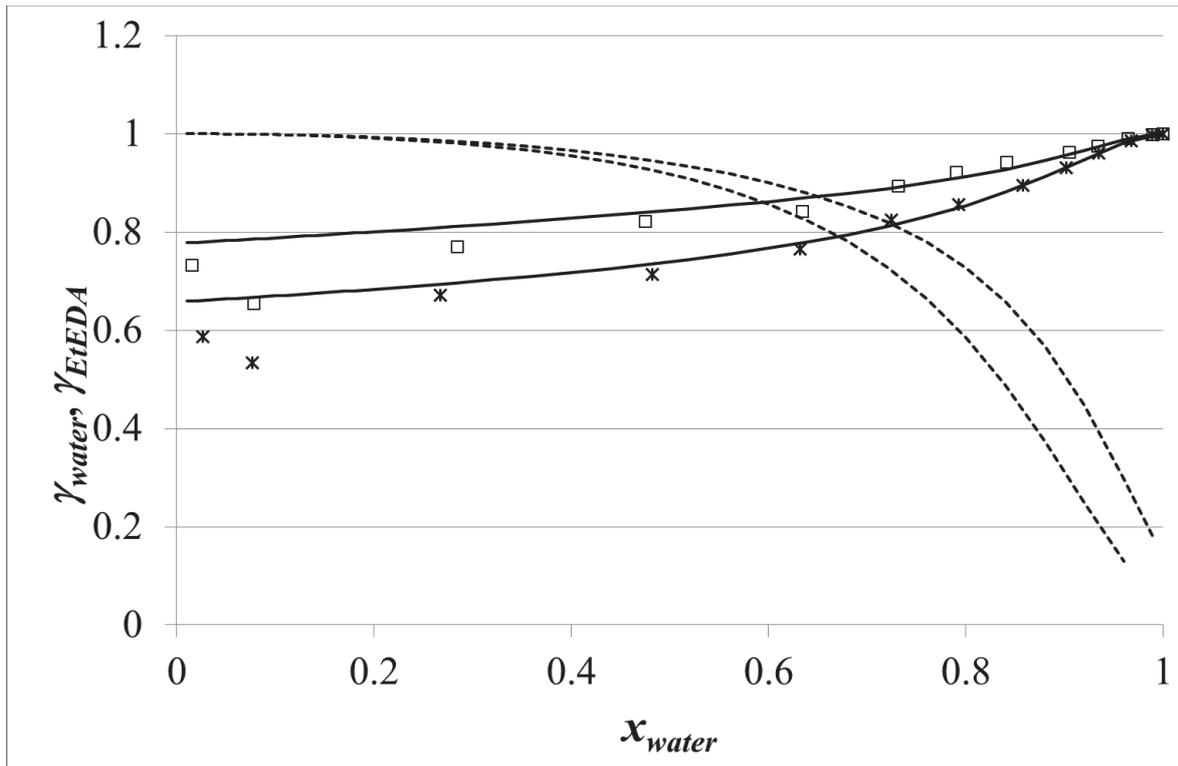


Figure 3.2. Activity factor of water (1) and ethylethylenediamine (2) vs. the molar fraction of water. Solid lines are γ_{water} calculated from UNIQUAC equation for 50 kPa (upper line) and 20 kPa (lower line). Dotted lines are γ_{EtEDA} calculated from UNIQUAC equation for 50 kPa (upper line) and 20 kPa (lower line). Points from experimental data at: \square 49.8 kPa and $*$ 19.8 kPa.

In the production of EDA, the separation of EtEDA from EDA is a problem as mentioned above. For many applications, EDA of high purity is required and it is very difficult to separate it completely from EtEDA. In Paper IV a tangential pinch was seen at the pressures investigated, see Figure 3.3.

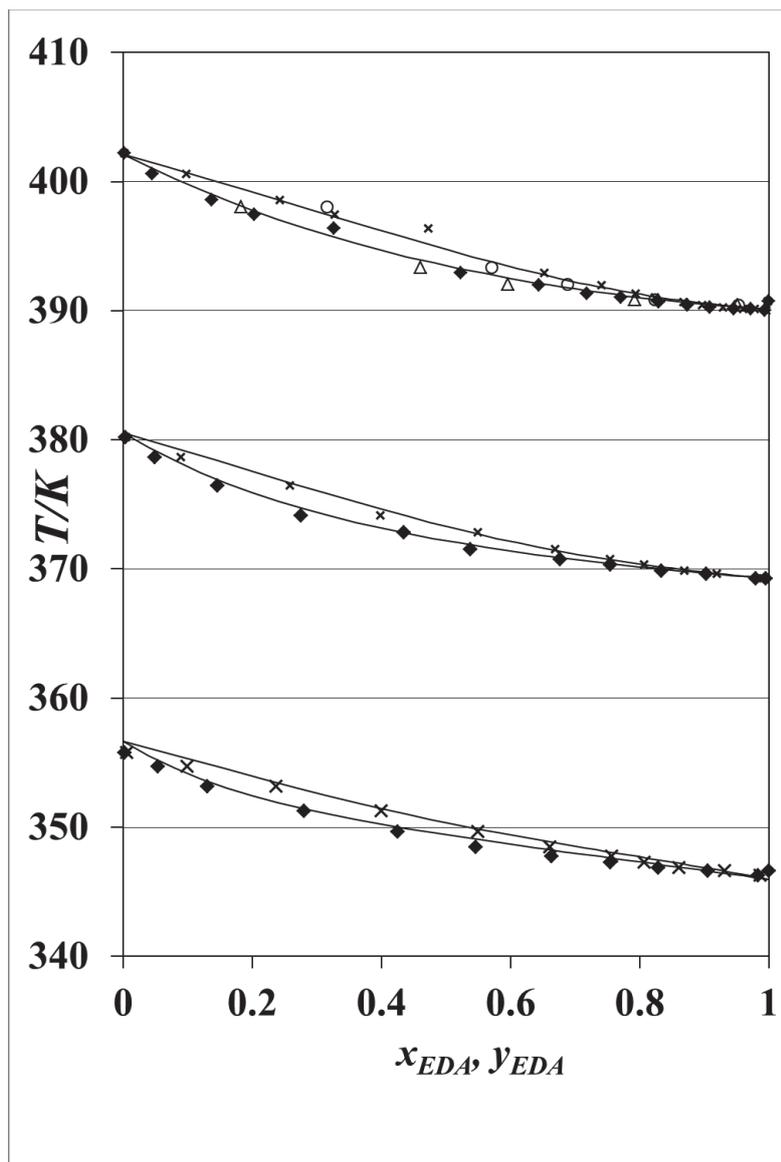


Figure 3.3 Experimental bubble points (\blacklozenge) and dew points (\times) for ethylenediamine(2) and ethylethylenediamine(3) at 20 kPa, 50 kPa and atmospheric pressure. Lines calculated with the UNIQUAC equation. Data from Cui et al (2007): bubble points(Δ) and dew points (\circ).

Cui et al. (2007) show that the volatility of EDA and EtEDA is reversed on the addition of ethylene glycol. Do et al. (2010) claim that the order of volatility between EDA and EtEDA can be reversed through “an azeotropic interaction”. They found that EtEDA was enriched in the top product of a column with a mixture of EDA, EtEDA and water with high water concentration.

This seems puzzling as EtEDA is the heaviest component both in its binary mixtures with EDA and with water. From a plot of the isotherms for the ternary mixture, it can be seen that there is a maximum in boiling point temperature along a line parallel to the axis from pure water to pure EDA and at the same time a minimum along a line perpendicular to that axis.

This is a saddle point azeotrope. It is predicted at a molar fraction of 0.24 of water, 0.62 of EDA and 0.14 of EtEDA and a temperature of 392.6 K.

How does this saddle point azeotrope influence VLE of the ternary? In Paper IV a plot of the univolatility lines and unidistribution lines is shown. It is reproduced here for the convenience of the reader as Figure 3.4. The relative volatility is defined as:

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j}$$

where K_i is the distribution coefficient of component i . Along a univolatility line, the relative volatility is one, and thus the two components are equally volatile. As the line is crossed, the volatility between component i and j is reversed. The distribution coefficient, K_i , is one for component i along the unidistribution line. When the distribution coefficient is greater than one, the component is enriched in the vapor phase. A binary azeotrope has one univolatility line that crosses the axis between the two components in a ternary diagram. The two unidistribution lines for the components involved also meet in that point. This can be seen for the azeotrope between EDA and water in Figure 3.4. In the ternary azeotrope, the three unidistribution lines and the three univolatility lines meet. The composition triangle is divided into regions of K-ranking (order of volatility) by the univolatility lines. These regions are shown in the plot with the most volatile component first and the heaviest last. In two regions EtEDA is the most volatile and in the upper part of the triangle (the water rich part) the volatility between EDA and EtEDA is reversed. This explains why Do et al (2010) found that the volatility of EDA and EtEDA was reversed in their mixture. The experimental data points for the ternary mixture are also marked in the ternary plot. The regions of K-ranking through which they pass are confirmed experimentally. However, some experimental points are almost on the α_{13} line and there the calculated and experimental results disagree for some of the points.

A plausible physical explanation to this ternary azeotrope is that the bulky ethyl-group in the EtEDA disturbs the strong interaction between EDA and water.

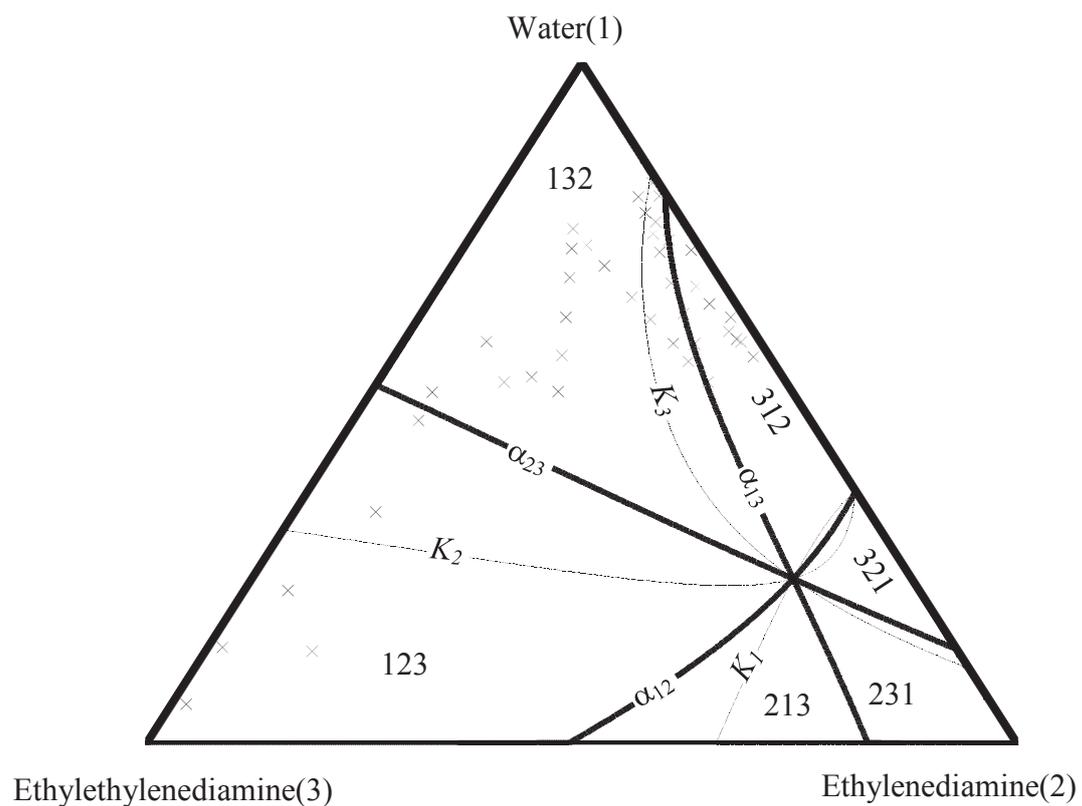


Figure 3.4 Univolatility lines and unidistribution lines for the ternary mixture of water EDA and EtEDA at one atmosphere. Regions of order of volatility are indicated in the figure.

4. Density of water and ethylenediamine

Knowledge of the density, ρ , of a mixture is both of practical and theoretical importance; the density is needed in the design of process equipment, can be used when fitting parameters to thermodynamic models and it can also be a convenient way of finding the composition of a binary mixture. From density data, the excess molar volume, V^E , can be calculated. It provides information on the structure and intermolecular forces in the mixture. According to Battini (1970), V^E can be used for testing theories of solution and for converting constant pressure properties into constant volume properties. The density measurements in this study are presented in Paper III.

4.1. Principle and procedure for the measurement

The densitometer used in this study is a vibrating tube apparatus from Anton Paar. The measuring principle is to measure the eigenfrequency of a U shaped tube brought to an undamped oscillation. The tube is filled with the mixture for which the density is sought and the frequency depends on the mass of the tube and its content. The temperature of the mixture and U-tube is kept constant by circulating water kept at a constant temperature in the double mantel of the insulated glass cell. In this study, nitrogen (gas) and bidistilled water was used for calibration. Ordinarily, air and water is used, but other liquids and gases can be used when calibrating as well. For the specific measurement in this study it was important to protect the mixtures containing ethylenediamine (EDA) from the air. For this reason an external pressure of 0.2 MPa of nitrogen gas was applied. Thus, instead of using air for the calibration, the nitrogen gas was used and any problems of deciding the humidity of the air were eliminated. When the mixtures were prepared by weighing in small glass bottles, the water was weighed in first. The bottles were then covered with a membrane before the EDA was added using a syringe. At high water content the mixture became very hot and without the membrane the evaporation would have been significant.

The density (ρ) of a sample is calculated from the frequency of the oscillation (τ) as:

$$\rho = \frac{(\tau^2 - B)}{A} \quad (4.1)$$

where A and B are calibration constants.

4.2 Density and departure from additivity

The results of the density measurements are show in Figure 4.1. As may be seen, there is a local maximum in density at low temperatures. Therefore, at room temperature, density measurements cannot be used to determine the composition for mixtures with high water content. According to Schmelzer and Quitzsch (1973), measurement of the refractive index can be used for determining the composition only at high water content, thus providing a complement to density measurements.

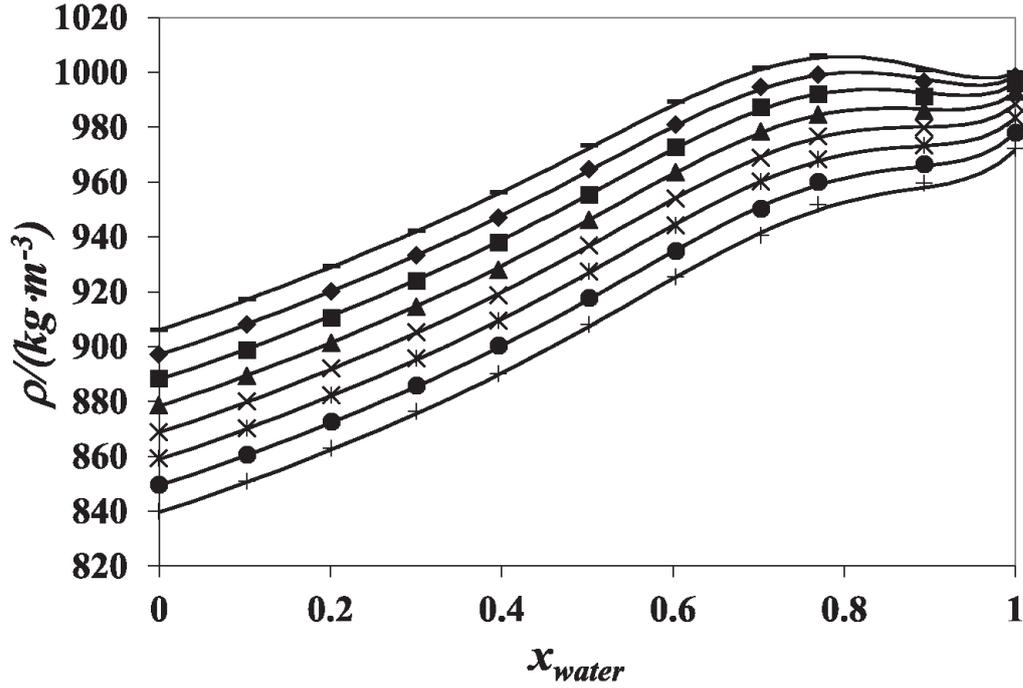


Figure 4.1. Density plotted versus the molar fraction of water for the binary ethylenediamine and water. Symbols as labeled in the figure for the measured data points and lines calculated from the Redlich-Kister model without temperature dependence for the excess molar volume and the models for the pure component densities found in Paper III. Symbols : experimental data from Paper IV for $- 283\text{K}$, $\blacklozenge 293\text{K}$, $\blacksquare 303\text{K}$, $\blacktriangle 313\text{K}$, $\times 323\text{K}$, $* 333\text{K}$, $\bullet 343\text{K}$, $+ 353\text{K}$.

Note that there was a misprint in the data by Valtz et al. (2006) and that a corrigendum was published in 2012 (Valtz et al. (2012)). The corrigendum also contains new AADs for the model presented in Paper III.

Kruglyak et al. (1980) define the departure from additivity for the density ($\Delta\rho / \text{kg/m}^3$):

$$\Delta\rho = \rho - \sum \rho_i z_i \quad (4.2)$$

where the apparent molar volume fraction (z_i)

$$z_i = \frac{X_i / \rho_i}{\sum_i \frac{X_i}{\rho_i}} \quad (4.3)$$

and X_i is the mass fraction of component i in the mixture. This density departure is plotted in figure 4.2. This departure is positive for all composition and temperatures. It has a maximum at a molar fraction of water of 0.69. The isotherms do not cross each other. The departure decreases with temperature. The difference between the highest and lowest temperature at the maximum is 8 kg/m^3 . This is modeled well by the V^E model without temperature dependent parameters and is thus attributed to differences in the pure component densities.

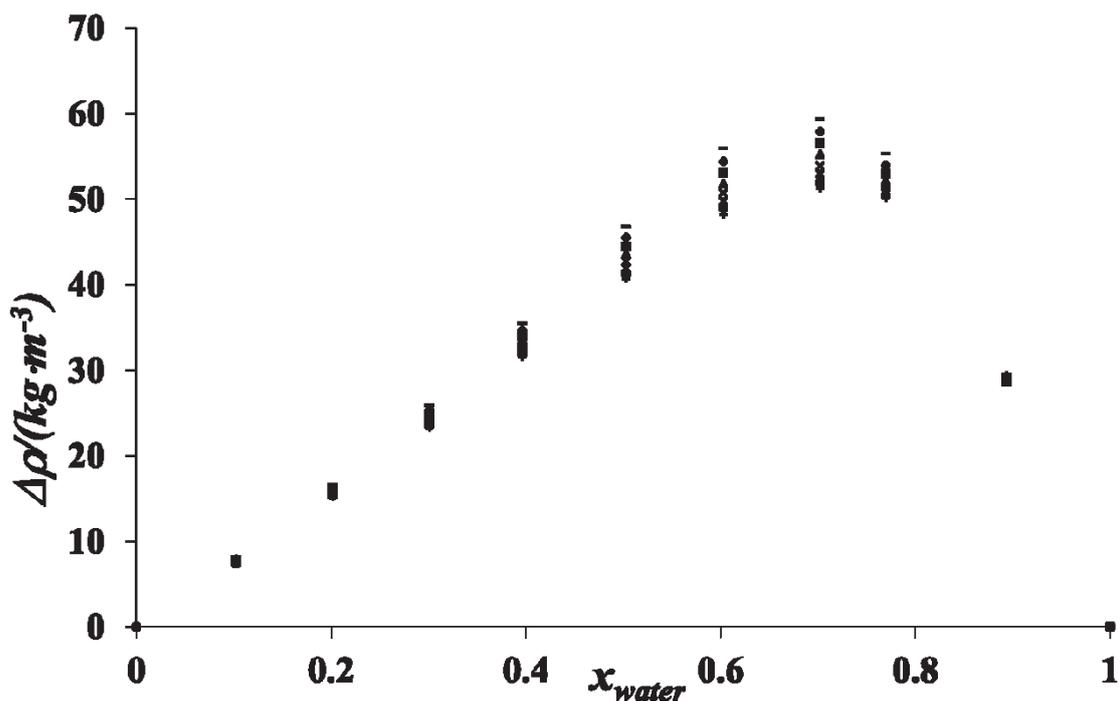


Figure 4.2 Density departure ($\Delta\rho$) versus molar fraction of water for the binary ethylenediamine and water. The isotherms do not cross each other. Symbols : experimental data from Paper IV for -283K , $\blacklozenge 293\text{K}$, $\blacksquare 303\text{K}$, $\blacktriangle 313\text{K}$, $\times 323\text{K}$, $* 333\text{K}$, $\bullet 343\text{K}$, $+ 353\text{K}$.

4.3 Excess molar volume

When two compounds are mixed, the total volume of the mixture can be different from the sum of the volumes of the two pure compounds. The difference is the so called excess molar volume (V^E). It is defined as:

$$V^E = V - \sum_i x_i V_i^\circ \quad (4.4)$$

That is, it is the difference between the molar volume of the mixture (V) and the sum of the pure component molar volumes (V_i°). For an ideal solution V^E is zero, and for a real solution it can be seen as a measure of the deviation from ideality. Positive values for V^E mean that mixing causes a volume expansion. This may be caused by dispersion forces, electrostatic repulsion between the species in the mixture, steric hindrance and unfitting geometry (Rowlinson and Swinton, 1982). Mixtures with one polar and one non-polar component often have a positive V^E (Rowlinson and Swinton, 1982). Negative V^E values, volume contraction upon mixing, can be caused by attraction forces between molecules and by molecules of one species fitting in caves between molecules of the other species (for example due to differences in size between the molecules). The attractive forces between species may be strong, such as ionic bonds and hydrogen bonds, or weaker such as dipole-dipole, dipole – induced dipole and London forces. Mixtures of n-alkanes often have a negative V^E increasing in magnitude with increasing temperature (Rowlinson and Swinton, 1982). Typically, mixtures of one polar and one non-polar compound have positive V^E . Several mixtures between a small polar

compound and a larger polar compound have negative V^E (Rowlinson and Swinton, 1982). The behaviour can however, be very complicated; V^E can switch from positive to negative over the composition range or even exhibit double maxima (carbon tetra chloride and benzene at 20° C, Battino, 1970). Most often the magnitude of V^E is small – at most one or two percent of the total volume, but mixtures of fluorocarbons exhibit up positive V^E values from two to ten percent of the total volume (Rowlinson and Swinton, 1982).

V^E data used to be obtained by direct measurement in a dilatometer, but as more accurate methods for density measurements appeared in the 1960s and 70s it is often calculated from density data nowadays. The excess molar volume was then calculated from the measured densities as:

$$V^E = \frac{\sum_i x_i M_i}{\rho} - \sum_i \frac{x_i M_i}{\rho_i} \quad (4.5)$$

For this study, the density of pure water was calculated from the expression found in Wasserdampftaffeln (Schmidt and Oldenburg, 1963) and the density of pure EDA from a third degree polynomial fitted to the pure component data measured in this study. This expression is found in Paper III.

The data is typically correlated by equations of the Redlich-Kister type with one equation for each isotherm. For EDA and water in the temperature range covered by this study, one and the same Redlich-Kister expression could describe the data. This expression and plots of the residuals are found in Paper III.

According to Battino (1970), exchanging the molar fraction in the Redlich-Kister expression for the apparent volume fraction (z_i in Equation d. 8) can increase the accuracy with the same number of parameters. This did not hold for the mixture of EDA and water.

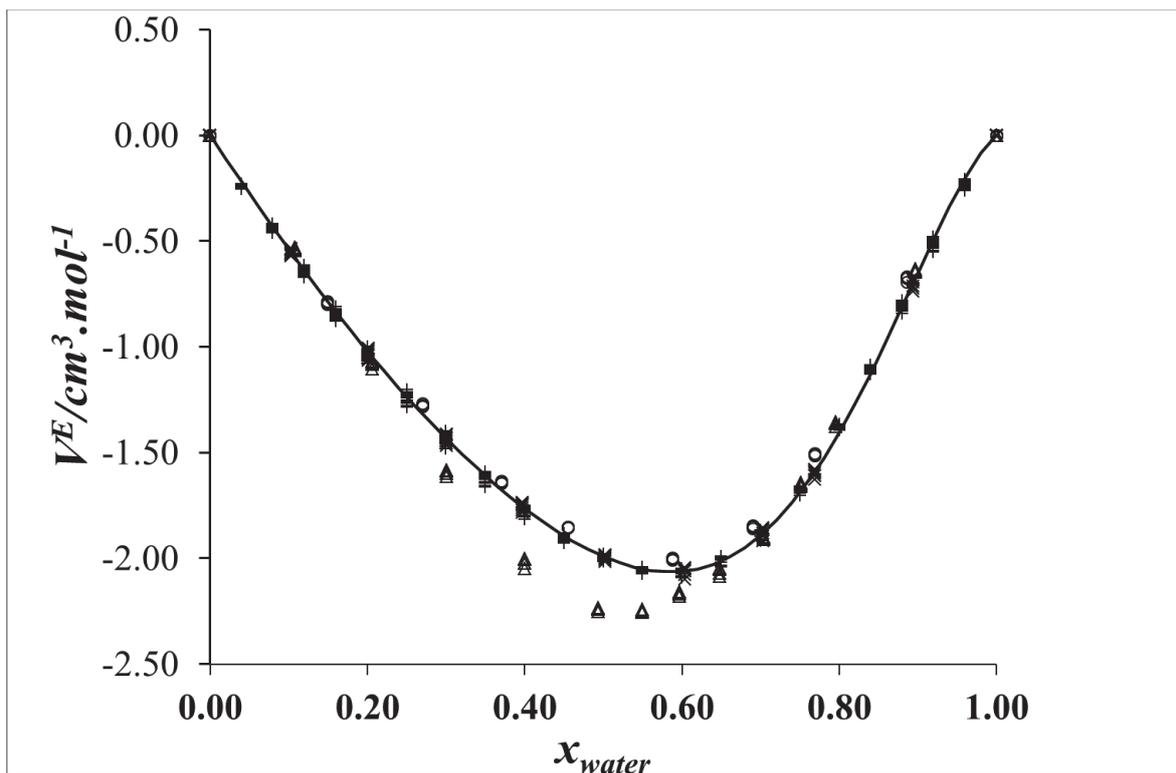


Figure d.3 Excess molar volume for water and EDA. Line calculated from Redlich-Kister expression and measured data from: X this study, \circ Kapadi et al. 2003, Δ Saleh et al 2005, and + Valtz et al. 2006.

The V^E for EDA and water is negative for all compositions as shown in Figure d.3. The curve vs. composition is slightly skewed with its minimum at about a molar fraction of water of 0.6. The magnitude is considerable. At e.g. $x_{\text{water}}=0.5$ and 25°C it is 2.23% of the total volume. Compare with water and ethanol at 25°C where the V^E minimum is $-1.1 \text{ cm}^3/\text{mol}$ (Benson and Kiyohara, 1980). A mixture with two nonpolar compounds that reach a similar magnitude, is n-nonane and n- $\text{C}_{62}\text{H}_{126}$ with $V^E=-2.51 \text{ cm}^3/\text{mol}$ (Battini, 1970). Aqueous solutions of other amines of similar magnitude are: water and diethylenetriamine (25°C) $-2.03 \text{ cm}^3/\text{mol}$; water and triethylene tetramine $-2.10 \text{ cm}^3/\text{mol}$ and water and tetraethylenepentamine $-2.21 \text{ cm}^3/\text{mol}$ (Rouleau and Thompson, 1962). Ethanolamine, which is like EDA but with one of the amine groups substituted for a hydroxyl group, has a minimum V^E of $-0.7 \text{ cm}^3/\text{mol}$ at 25°C (Maham et al. 1994).

V^E in the mixture of water and EDA varies little with temperature. However, the isotherms cross each other. In the density departure, the isotherms did not cross. For the aqueous mixtures of alkanolamines, V^E increased (that is, became less negative, with a decreasing magnitude) as the temperature increased (Chan et al. 2002). Figure d.4 shows the variation with temperature for five concentrations. For all concentrations, V^E first increases with temperature and then decreases after having reached a maximum. The location of the maximum is shifted towards higher temperatures as the water content increases, but then shifts back again as the minimum in the V^E curve is passed. The change in V^E with the temperature is moderate and even lower at higher temperatures. Thus extrapolations appear to

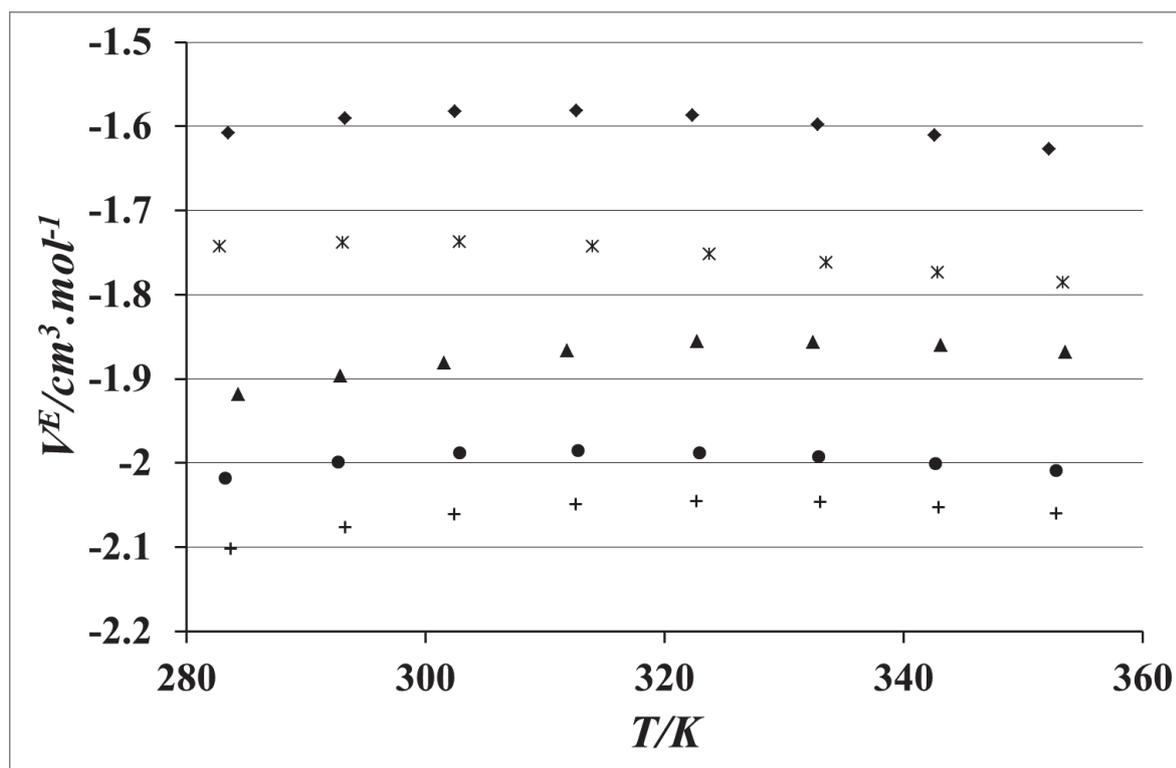


Figure 4.4 Excess volume (V^E) versus temperature for following molar fraction of water: *0.4, ○0.5, +0.6, Δ0.7 and ♦ 0.77. Experimental data from Paper III.

4.4 Partial molar volumes

The partial molar excess volumes show the contribution to the total molar excess volume from each component. They are defined as:

$$V_i^E = \left(\frac{\partial (nV^E)}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

Thus:

$$V_i^E = V_i - V_i^O$$

That is: the partial molar excess volume is difference between the partial molar volume of component i in the mixture (V_i) and the molar volume of pure component i (V_i^O). The partial molar volumes of EDA and water in the mixture, calculated from derivatives of the Redlich – Kister expression for V^E , are found in Paper III. The curve for the partial molar excess volume of EDA has a minimum close to pure water. This resembles the behavior of methanol and water (Benson and Kiyohara, 1980).

The V_i^E curve, being a derivative of the Redlich-Kister expression, is very sensitive to its parametrisation. Also, as there are no measured values for the dilute regions, extrapolation to infinite dilution is not safe. Compare the curve in Paper III with Figure d.7 where the partial molar excess volumes are obtained from the Redlich –Kister expression by Valtz et al., 2006

for 298.15K. Valtz et al. 2006 have one measured value at $x_{\text{water}}=0.04$ that causes the strong dive of the curve for $V_{\text{H}_2\text{O}}^E$ close to pure EDA. One alternative way of finding the partial molar excess volumes at infinite dilution is to plot $V^E/x_{\text{water}}x_{\text{EDA}}$ versus x_{water} and extrapolate the curve to the intercept with the axis. From such plots, the influence of the measured value at $x_{\text{water}}=0.04$ can be seen clearly.

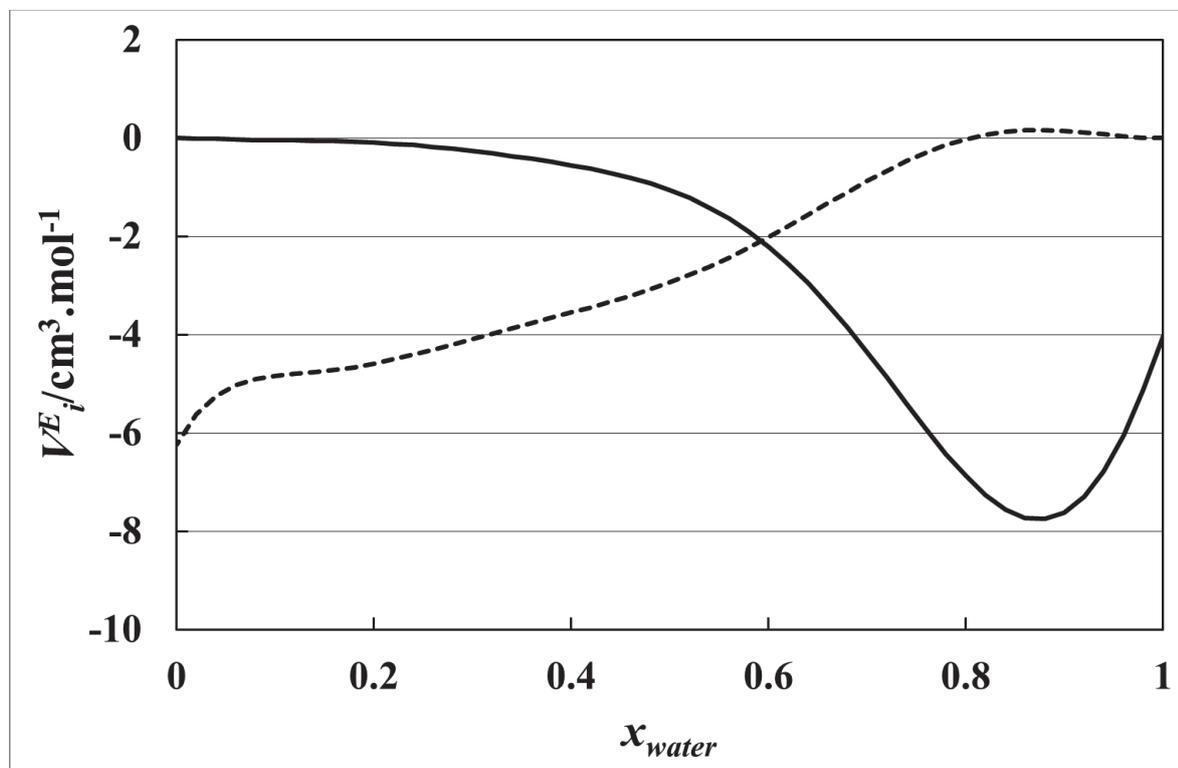


Figure 4.5 Partial molar excess volume of water (dotted line) and EDA (solid line) calculated from derivatives of the Redlich-Kister equation with parameters Valtz et al. 2006 at $T=298.15\text{K}$.

4.5 Discussion of interpretations of the volumetric behavior

”Of the various thermodynamic functions for the mixing process, the volume change on mixing at constant pressure... is one of the most interesting, yet one of the least understood.” (Hildebrand and Scott, 1962). The difficulty in understanding V^E data can be seen in the diverse interpretations made for EDA and water in the literature.

4.5.1 V^E is negative and large

As mentioned in section 4.3 the volume contraction in the system is considerable. The causes for this that have been suggested in literature will be discussed in the following sections.

4.5.1.1 Hydrogen bonding

EDA has two amine groups that can be involved in hydrogen bonds and water is well-known for hydrogen bonding. Thus, for V^E of EDA and water, it is obvious to attribute at least part of the contraction to hydrogen bonding – and most of the authors do so (Cheng et al., 1993, Saleh et al. 2005, Kapadi et al. 2003, Valtz et al. 2006). Kapadi et al. (2003) also measured the viscosity of EDA and water mixtures and found the Gibbs excess energy of activation is positive. This indicates strong hydrogen bonding (Kapadi et al. 2003). In systems dominated by hydrogen bonding, V^E typically increases (becomes less negative) with the temperature (Valtz et al. 2006). The hydrogen bonded network is thought to be disturbed by thermal agitation. As was shown in Figure 4.4 the excess volume passes through a maximum in the temperature range covered in this study. One possible interpretation is that the initial increase in temperature is caused by the temperature sensitive hydrogen bonds and the later decrease is caused by geometry effects, just as for nonpolar systems.

4.5.1.2 Geometry effects

The partial molar excess volume at infinite dilution for both EDA in water and water in EDA are negative. Valtz et al. 2006 and Chan et al. 2002 (alkanolamines) claim that this is due to geometry effects – that there is “void space” in the pure components due to hydrogen bonding between like molecules. In systems where geometrical effects, small molecules fitting in the holes between larger molecules, are important, such as nonpolar compounds of different size, V^E typically decreases (becomes more negative) with the temperature (Rowlinson and Swinton, 1982).

4.5.1.3. Hydrophobic effects

Saleh et al. (2005) claim that hydrophobic effects are important in creating the volume contraction and that the position of the minimum in the curve is found where hydrophobic hydration is replaced by hydrophobic interaction. According to Cheng et al. (1993), hydrophobic effects can be divided into hydrophobic hydration and hydrophobic interaction. Hydrophobic hydration is the stabilization of the hydrogen bonded network of water caused by a nonpolar solute. Hydrophobic interaction causes the nonpolar part of the solute to aggregate or form chains. According to Cheng et al. (1993), hydrophobic features can be observed in the dilute region for aqueous solutions of some organic cosolvents. In their study, Cheng et al. (1993), use what they call the “inverted Kirkwood-Buff” theory to generate radial distribution functions from density and VLE data for EDA and water. They found that hydrophobic effects were not present and claim that this is because the strong interaction between water and the amine groups inhibit the formation of clathrate-like hydrogen bonded network around the nonpolar part of EDA. It should be kept in mind that their calculation of the radial distribution function is based on the data available for the system at that time and that very little data for the dilute region are available. However, their conclusion that

hydrophobic effects are of small importance in this very hydrophilic system, seems reasonable (Kjellander, 2011). Valtz et al. (2006), referring to Saleh et al. (2005), claim that hydrophobic hydration causes the partial molar volumes at infinite dilution not be temperature dependent. However, as hydrophobic effects are entropy effects they are typically temperature dependent (Kjellander, 2011).

4.5.1.4 Formation of hydrates

Kruglyak et al. (1980) claim that the maximum in departure from additivity of the density around $x_{\text{water}}=0.7$ indicates that the 2-hydrate of EDA is dominating ($\text{EDA} \cdot 2 \text{H}_2\text{O}$), and that the minimum of V^E around a molar fraction of water of 0.6 may be interpreted as the presence of both the 2-hydrate and the 1-hydrate. However, these two curves are only transformations of each other. In order to know if these hydrates are formed, other data, such as spectroscopic data, would be needed. Furthermore Boo 2001, claim that the most stable hydrate is $\text{EDA}^+ \cdot 3\text{H}_2\text{O}$.

EDA is a strong base with $\text{pKb}_1= 3.83$ at 298.15K (Keller and Edwards, 1952). According to Boo, 2001, the most stable and energetically favored configuration for EDA is the protonated EDA^+ with three water molecules bonded to the NH_3^+ moieties. He claims that structures with water molecules bonded to $-\text{NH}_2$ are either unstable or not as favored in energy.

4.5.2. The minimum in partial molar volume

The partial molar excess volume for EDA has a minimum close to pure water (see Figures 4.5 and in Paper IV). This indicates that the EDA molecules enforce each other: V_i^E becomes more negative as more molecules are added. The behaviour has to be an energy effect and not simply a geometry effect. When mixtures with high water content were prepared they became very hot. That is also an indication that the addition of EDA to water is favored energetically.

Benson and Kiyohara (1980) interpret the partial molar excess volume curve for alcohol-water systems, with the same kind of minimum as shown in Figure 4.5: "The occurrence of such a minimum has been attributed to a balance between the effects of interstitial solution of alcohol molecules with accompanying enhancement of the ice.-like structure in the water, and a breaking of this structure with increasing concentration of the alcohol." It should however be kept in mind that the empty spaces created by the hydrogen bonded water network are small: smaller than a water molecule (Kjellander, 2011).

4.5.3 Disappearing local maximum in density

Local maxima in density similar to that of water and EDA (Figure 4.1), disappearing as the temperature is increased, were observed by Chan et al. (2002) for aqueous mixtures of some

alkanolamines. Chan et al. (2002) interpreted this behavior as a competition between structuring processes, causing a volume contraction, and thermal agitation. In their case, magnitude of the excess molar volume decreased with temperature. Note that in the case of EDA and water, the disappearing local maximum in density, is modeled well by the Redlich-Kister expression, without any temperature dependence, combined with the pure component densities (Figure d.1.). It seems that the difference in the temperature behavior of the density of the pure components, superimposed on a V^E that does not depend on the temperature, causes the disappearing local maximum for EDA and water.

5. MHV2 and h^E prediction for water, EDA and EtEDA

For the aqueous mixture of EDA and EtEDA, no h^E data that covers the entire composition range could be found in the literature. Cross-prediction of h^E , as performed in Paper I, gives an idea of what can be expected. If the predictions are reasonable, this is an indication that the temperature dependence of the VLE model is qualitatively correct.

The UNIQUAC equation presented in Paper IV can be incorporated in an equation of state, here the SRK equation, through the MHV2 mixing rule. Sometimes there is a discrepancy between the equation of state model and the g^E -model incorporated. A comparison is thus given here to find out if the equation of state model is reliable for this system.

5.1 Excess enthalpy predicted

With the UNIQUAC model from Paper IV, h^E curves for the binary mixtures can be predicted as described in Paper I. Remember that the cross-prediction of h^E from VLE with temperature dependent parameters is not very reliable. The qualitative results for water and EDA (Figure 5.1) and for water and EtEDA (Figure 5.2) agree with what could be expected for aqueous solutions of polyamines. According to Rowlinson and Swinton (1982), the bonds between the solute and water for these systems, are so strong that the excess enthalpy is more negative than the absolute temperatures times the excess entropy, causing also the Gibbs free energy to be negative. The Gibbs free excess energy showed in the figures was calculated from the UNIQUAC model in Paper IV as well. From observations made during the experiments, the curve for EDA-water should be skewed with the minimum closer to the pure water end. The results for EDA and EtEDA (Figure 5.3) are complicated and appear strange. Even though this probably is caused partially by problems with the UNIQUAC, as seen in Paper I, it is likely to indicate that there is a problem with the vapor pressure that forces the temperature dependency of the UNIQUAC parameters to be wrong.

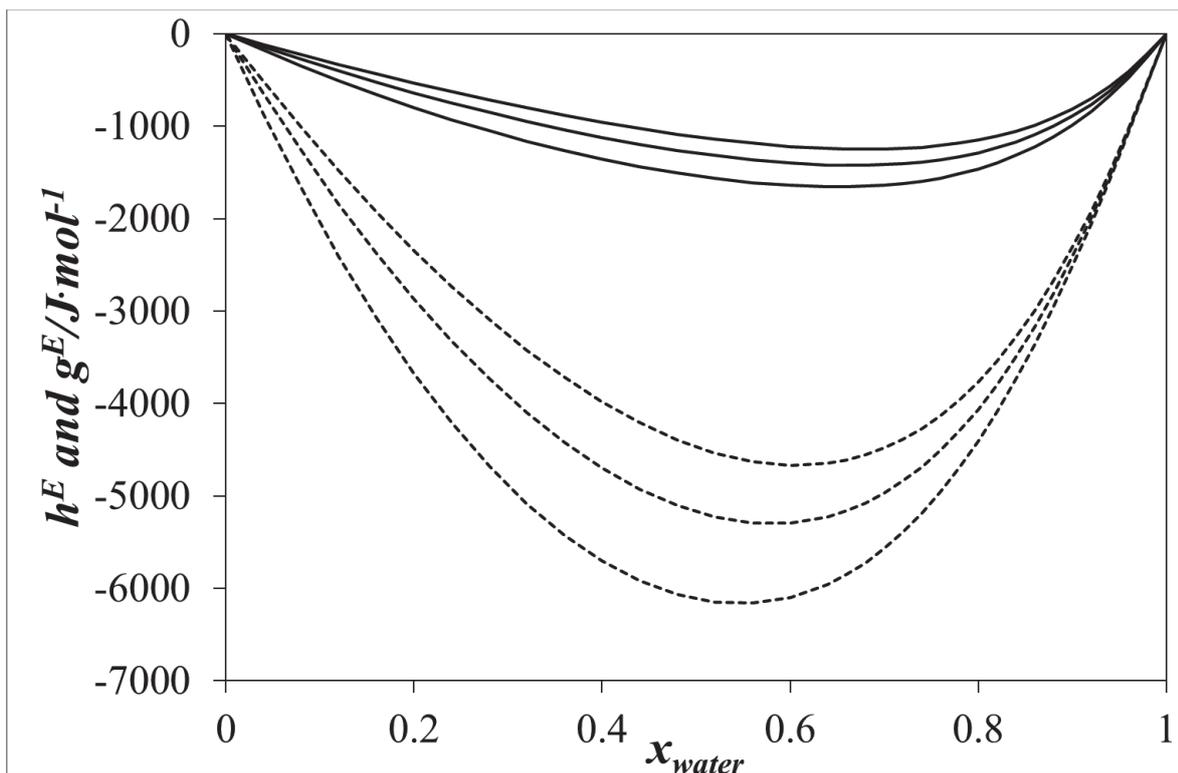


Figure 5.1 Predicted Gibbs excess energy (solid lines) and excess enthalpy (dashed lines) for water and ethylenediamine at 20 kPa, 50 kPa and atmospheric pressure versus the molar fraction of water. The Gibbs excess energy and the excess enthalpy values are more negative for the lower pressures.

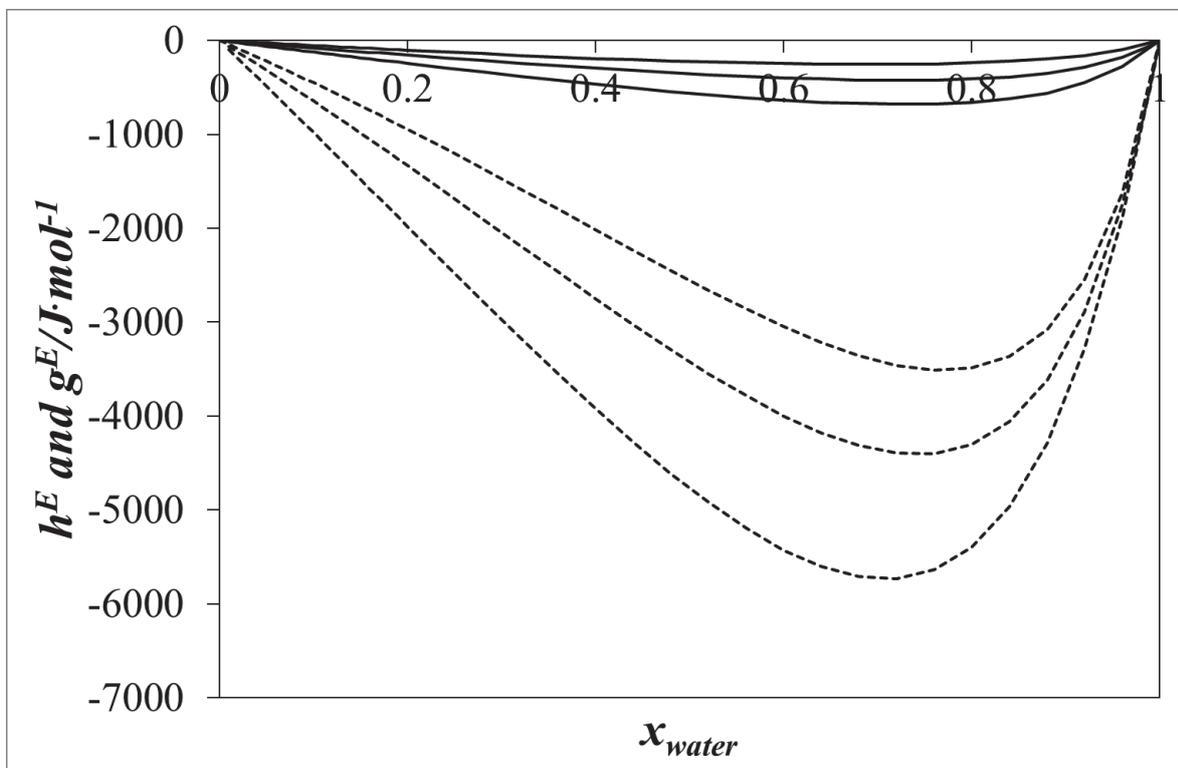


Figure 5.2 Predicted Gibbs excess energy (solid lines) and excess enthalpy (dashed lines) for water and ethylethylenediamine at 20 kPa, 50 kPa and atmospheric pressure versus the molar

fraction of water. The Gibbs excess energy and the excess enthalpy values are more negative for the lower pressures.

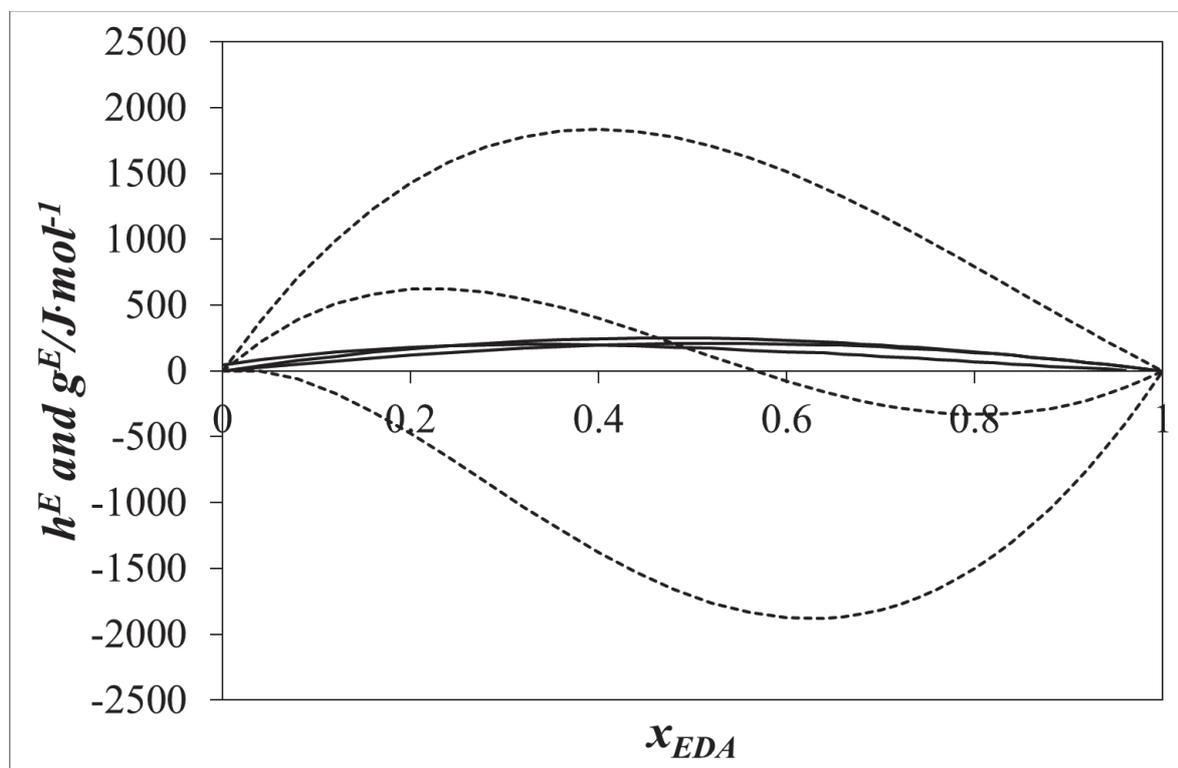


Figure 5.3 Predicted Gibbs excess energy (solid lines) and excess enthalpy (dashed lines) for ethylenediamine and ethylethylenediamine at 20 kPa, 50 kPa and atmospheric pressure versus the molar fraction of water. The Gibbs excess energy and the excess enthalpy are more negative for the lower pressures.

5.2 Comparison with the MHV2

In Paper IV, the UNIQUAC model was used to correlate the data. Here, a brief comparison with the SRK equation of state with the MHV2 mixing rule will be given. The g^E model used in the MHV2 calculations is the UNIQUAC equation with the parameters presented in Paper IV. Mathias-Copeman parameters were estimated in the same way as in Paper II for EDA and EtEDA and are found in Table 5.1. The vapour pressure data used in the parameter estimation for EDA are those by Hieber and Woerner (1934). For water, the vapour pressure data was from Osborn and Douslin (1974) and for EtEDA the measurements from Paper IV were used. The critical temperature and pressure for EDA were measured by Wilson et al. (1996). For EtEDA they were predicted with the Ambrose method as that appeared to be the most accurate according to the study presented in the appendix.

Table 5.1 Critical data and Mathias-Copeman parameters for water, EDA and EtEDA.

	Water	Ethylenediamine	Ethylethylenediamine
T_c/K	647.3	613.1	583
P_c/Pa	$22.12 \cdot 10^6$	$6.707 \cdot 10^6$	$4.06 \cdot 10^6$
c_1	1.057	1.05989	1.36362
c_2	-0.465	-0.67094	-1.0352
c_3	0.345	1.90814	1.96507

The results of bubble-point pressure calculations with the UNIQUAC equation and the MHV2 were very similar for these three binary systems. In Table 4.2, the absolute average deviations between experimental data and the models and between the two models are given. The difference between UNIQUAC and MHV2 in calculated pressure is greatest close to pure EDA and then falls proportionally as pure water or EtEDA is approached. Thus, it seems that the difference stems from a difference in calculated vapour pressure for pure EDA.

Table 5.1 Absolute average deviations in the bubble-point pressure. Pressure (P) in kPa and vapour phase composition in molar fraction.

	$\frac{P^{exp} - P^{UNIQUAC}}{P^{UNIQUAC}}$	$\frac{P^{exp} - P^{MHV2}}{P^{MHV2}}$	$\frac{P^{UNIQUAC} - P^{MHV2}}{P^{MHV2}}$	$\frac{y_1^{exp} - y_1^{UNIQUAC}}{y_1^{UNIQUAC}}$	$\frac{y_1^{exp} - y_1^{MHV2}}{y_1^{MHV2}}$	$\frac{y_1^{UNIQUAC} - y_1^{MHV2}}{y_1^{MHV2}}$
Water-EDA	1.55	1.94	0.53	0.013	0.013	0.0008
Water-EtEDA	0.95	0.94	0.04	0.008	0.008	0.0010
EDA-EtEDA	0.57	0.92	0.54	0.016	0.014	0.0052

Predictions with the SRK equation of state and MHV2 mixing rule with UNIQUAC parameters from the VLE measurements do not give a good representation of the excess molar volume, see Figure 5.4. This is to be expected as the SRK equation of state does not reproduce the liquid densities well, especially not for water.

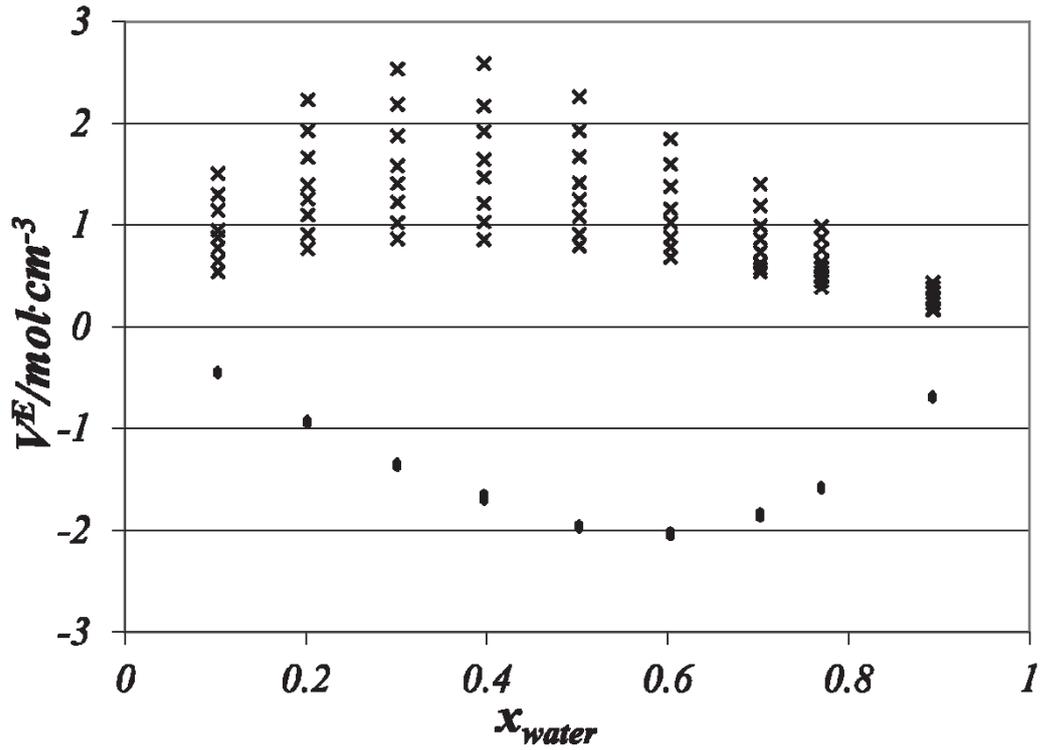


Figure 5.4 Excess molar volume for water and ethylenediamine versus the molar fraction of water: x the SRK equation of state with MHV2 mixing rules and \blacklozenge experimental data.

6. Conclusions

The UNIQUAC equation produced better cross-predictions of h^E data with parameters from estimated from VLE data in the DECHEMA data collection series, compared to the other local composition models.

In order to model skewed h^E curves and h^E values of higher amplitude, more flexibility had to be added to the UNIQUAC equation. With a linear temperature dependency in both binary interaction parameters, a reasonable fit was obtained at an acceptable numerical stability. Simultaneous regression of both h^E and VLE data improves the numerical stability.

There is a lack of fit in the MHV2 mixing rule due to the approximation that makes the mixing rule explicit. This lack of fit cancelled out a common error in the temperature dependency of the UNIQUAC model with DECHEMA parameters, resulting in h^E predictions from the MHV2 model that were better than those from the UNIQUAC model incorporated in the MHV2 model.

When VLE and enthalpy calculations are to be made with the same g^E model or g^E mixing rule, estimating binary interaction parameters simultaneously from both kinds of data, gives the best result.

The density of the mixture of water and EDA was measured and found to have a local maximum at high water contents for temperatures below 300K. Thus, the composition of the binary mixture cannot be determined by measuring the density in that region.

The excess molar volume for the mixture of water and EDA is negative and has unusually great amplitude, indicating strong intermolecular forces. Furthermore, it is relatively independent of the temperature, which makes extrapolation reasonable.

VLE data were measured for the binary mixtures of water EDA and EtEDA and for the ternary mixture. The binary mixture of water and EDA has a maximum boiling azeotrope at atmospheric pressures and below.

The binary mixture of EDA and EtEDA has a zeotropic pinch close to pure EDA, making it very difficult to remove EtEDA by distillation.

The ternary mixture of water, EDA and EtEDA has a saddle point azeotrope at a molar fraction of 0.24 of water, 0.62 of EDA and 0.14 of EtEDA and a temperature of 392.6 K at atmospheric pressure. In both its binary mixtures, EtEDA is always the heaviest component, but due to the ternary azeotrope, it is the most volatile component in a region around the binary azeotrope for water and EDA. This can be used to avoid the difficult separation of EtEDA from almost pure EDA.

The Thodos Gomes method for polar compounds performed better than that for hydrogen bonding compounds in vapour pressure predictions for the amines. The predictions for diamines were more reliable than those for the ethanolamines. The Ambrose method for prediction of critical temperature and pressure gave the most reliable predictions for the diamines. Again the predictions for ethanolamines were uncertain.

7. Future work

Measurements of the excess enthalpy for water and EDA, water and EtEDA and EDA and EtEDA are needed. These would make the UNIQUAC model for the systems more reliable and would add to the understanding of the intermolecular interactions of the systems.

Measurements of the density of mixtures of water and EtEDA are desirable. These could be compared to those of water and EDA and would add to the understanding of the system.

In the parameter estimation for all the binaries in Paper IV, the vapor pressures are possible problems. It is known that the vapour pressure has to be known to a high accuracy. Thus, new measurements of the vapor pressure of the pure diamines are needed.

New cubic equations of state are appearing. Can the e.g. the CPA equation of state (Kontogeorgis et al. 1996) model the density and excess molar volume of water and EDA?

In new VLE measurements of EDA and water, the composition of the mixture can be determined by density measurements for water molar fractions below 0.5 and by measurement of the refractive index above 0.5. This could increase the precision in the determination of the composition.

The reliability and consistency of the g^E model are essential to calculations with the g^E mixing rules. It is thus important to develop the g^E models of today, to make them consistent with findings from molecular simulation and to enable crossprediction of h^E , VLE and LLE.

The g^E mixing rules need to be modified to fit into the theoretical framework of van der Waals theory. With the explicit zero pressure mixing rule, the g^E of the gas phase has been found to be influenced too much by the liquid phase g^E (Michelsen and Heidemann, 1996) and the second virial coefficients do not have a quadratic dependency in composition.

Nomenclature

a	equation of state energy parameter	
A	molar Helmholtz energy	J/mol
b	equation of state covolume parameter	m ³ /mol
B	second virial coefficient	
c	Mathias-Copeman parameters	
g	molar Gibbs free energy	J/mol
h	molar enthalpy	J/mol
k_{ij}	binary interaction parameter	
l_{ij}	binary interaction parameter	
M	molar mass	kg/mol
n	amount of substance	mol
P	pressure	Pa
q	auxiliary function	
R	gas constant	
T	temperature	K
s	entropy	J/(mol·K)
u	inverse packing fraction	
V	molar volume	m ³ /mol
x	molar fraction, liquid phase	
y	molar fraction, vapour phase	
z	volume fraction	

Greek letters

α	parameter	
γ	activity coefficient	
ρ	density	m^3/kg
ϕ	fugacity coefficient	
τ	frequency of oscillation	1/s

Superscript

E	excess property
l	liquid
r	residual
v	vapour
$^{\circ}$	ideal state
calc	calculated
exp	experimental

Subscript

c	critical
i	component
j	component
k	component

r	reduced
eos	equation of state
γ	activity coefficient model
∞	infinity

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Appendix 1.

Vapor pressure prediction methods compared for some amines

It is essential to VLE calculations that the vapor pressure of the pure components is well known. For many amines, there is a lack of experimental data and prediction methods need to be used. In a preliminary study, the ability of the Clapeyron (Reid et al. 1987), Thodos-Gomez for hydrogenbonding compounds (Gomez-Nieto and Thodos, 1977a, 1977b, 1978), Thodos-Gomez for polar compounds (Gomez-Nieto and Thodos, 1977a, 1977b, 1978) and Lee-Kesler (Lee and Kesler, 1975) prediction methods were compared. As critical data are not always available for a compound, a comparison of three prediction methods was included and the results of using these in the vapor pressure prediction methods shown. The methods are the Ambrose method (Ambrose 1978, 1979), the Joback modification of Lydersen's method (Joback, 1984) and Fedors method (critical temperature only) (Fedors, 1982). For two amines the boiling point was varied in order to see how this influences the predicted vapor pressure. The experimental data used for comparison is for:

*EDA from Hieber and Woerner, 1934

*MEA from Kapteina et al. 2005 and Tochigi et al. 1999

*MEDA from Olson 2001

*EEDA presented in Paper IV. A comparison with the data by Cui et al. (2007) is also included.

The normal boiling points of the compounds here were taken from literature (EDA and MEA) or from the limits given by the manufacturers (MEDA and EEDA). Jobacks (1984) method for approximation of normal boiling temperature yields good results for EDA (388.22K where the Reid et al. (1987) states 390.4K) and MEDA (389.74 K where Olson states 388.9K). For EEDA the deviation is within what can be expected according to Reid et al. (1987) (412.62K where the measurements showed 403K) but for MEA the prediction was not good (408.87K instead of 443.5K (Reid et al. 1987)). Similar results are obtained for diethanolamine (prediction 525K, literature 542K).

The critical temperatures estimated are compared in Table 4.2. As may be seen, the methods by Ambrose and Joback give similar results for the all the amines, whereas Fedors methods deviated more, as could be expected (Reid et al. 1987). All three estimation methods give poor results for MEA. Ambroses method overpredicted the critical pressure by 70% and Jobacks by 41%.

Table 4.2. Critical temperatures (T_c /K) from Reid et al and estimated by Ambroses, Jobacks and Fedors methods. Normal boiling points from the literature (known) are used for EDA and MEA. The low and high end of product specification used for MEDA and EEDA.

	EDA	MEDA	EEDA	MEA
known	593			614
Ambrose known/low T_b	592	574	583	666

Ambrose high T_b		577	586	
Joback known/low T_b	592	574	582	636
Joback high T_b		577	585	
Fedor	573	579	603	594

The results for the prediction methods are found in Table 2. The method by Thodos and Gomez for polar substances was the most accurate method for the compounds in this study. The method presented by Thodos and Gomez for hydrogen-bonding substances gave the largest residuals. According to Reid et al. 1987, it is suitable for alcohols but not for ammonia. It seems that this holds for amines as well. The Lee-Kesler method underpredicted the vapor pressure typically by slightly more than 10% at low pressures. This is expected below the normal boiling point (Reid et al. 1987). All the methods used give a correct value for the vapor pressure at the normal boiling point, as they are fitted to that point. The predictions are sensitive to errors in critical temperature, in normal boiling point and, to less extent, in the critical pressure as seen in Table 2.

Table 4.3 Root mean square deviation (RMSD/kPa) of the vapor pressure predictions to the experimental data.

	TC	PC	Boiling point	EDA	MEA	MEDA	EEDA
Clapeyron	Literature	literature	literature	0.25	0.14		
	Ambrose	Ambrose	literature/low	0.24	0.33	1.68	1.13
	Ambrose	Ambrose	high			0.38	0.71
	Joback	Joback	literature/low	0.28	0.14	1.70	1.01
	Joback	Joback	high			0.40	0.69
	Fedor	Ambrose	literature/low	0.12	0.68	1.83	1.82
	Fedor	Ambrose	high			0.45	1.09
	Fedor	Joback	literature/low	0.10	0.53	1.85	1.69
	Fedor	Joback	high			0.47	0.99
Gomez	Literature	literature	literature	0.45	0.35		
	Ambrose	Ambrose	literature/low	0.45	0.33	1.35	0.87
	Ambrose	Ambrose	high			1.58	1.69
	Joback	Joback	literature/low	0.41	0.42	1.34	0.98
	Joback	Joback	high			1.56	1.82
	Fedor	Ambrose	literature/low	0.66	1.05	1.30	0.55
	Fedor	Ambrose	high			1.52	1.29
	Fedor	Joback	literature/low	0.61	0.91	1.29	0.61
	Fedor	Joback	high			1.49	1.41
Lee	Literature	literature	literature	0.20	0.23		
	Ambrose	Ambrose	literature/low	0.20	0.06	1.22	0.53

	Ambrose	Ambrose	high			0.71	0.90
	Joback	Joback	literature/low	0.15	0.25	1.22	0.50
	Joback	Joback	high			0.69	1.03
	Fedor	Ambrose	literature/low	0.52	1.03	1.28	1.14
	Fedor	Ambrose	high			0.63	0.63
	Fedor	Joback	literature/low	0.46	0.88	1.29	1.01
	Fedor	Joback	high			0.60	0.63
Thodos Gomez polar	Literature	literature	literature	0.07	0.06		
	Ambrose	Ambrose	literature/low	0.07	0.12	1.36	0.76
	Ambrose	Ambrose	high			0.30	0.69
	Joback	Joback	literature/low	0.07	0.07	1.37	0.66
	Joback	Joback	high			0.29	0.76
	Fedor	Ambrose	literature/low	0.30	0.81	1.46	1.35
	Fedor	Ambrose	high			0.25	0.72
	Fedor	Joback	literature/low	0.25	0.66	1.48	1.23
	Fedor	Joback	high			0.23	0.67

Cui et al. 2007 published a measurement series for the vapor pressure of EtEDA. The data do not agree with those in Paper IV except for around the normal boiling point. They deviate from the Antoine equation in Paper IV in the same way as from the prediction methods. Below the normal boiling point, the vapor pressure was as much as 20 kPa too high and above the normal boiling point it dives down quickly.

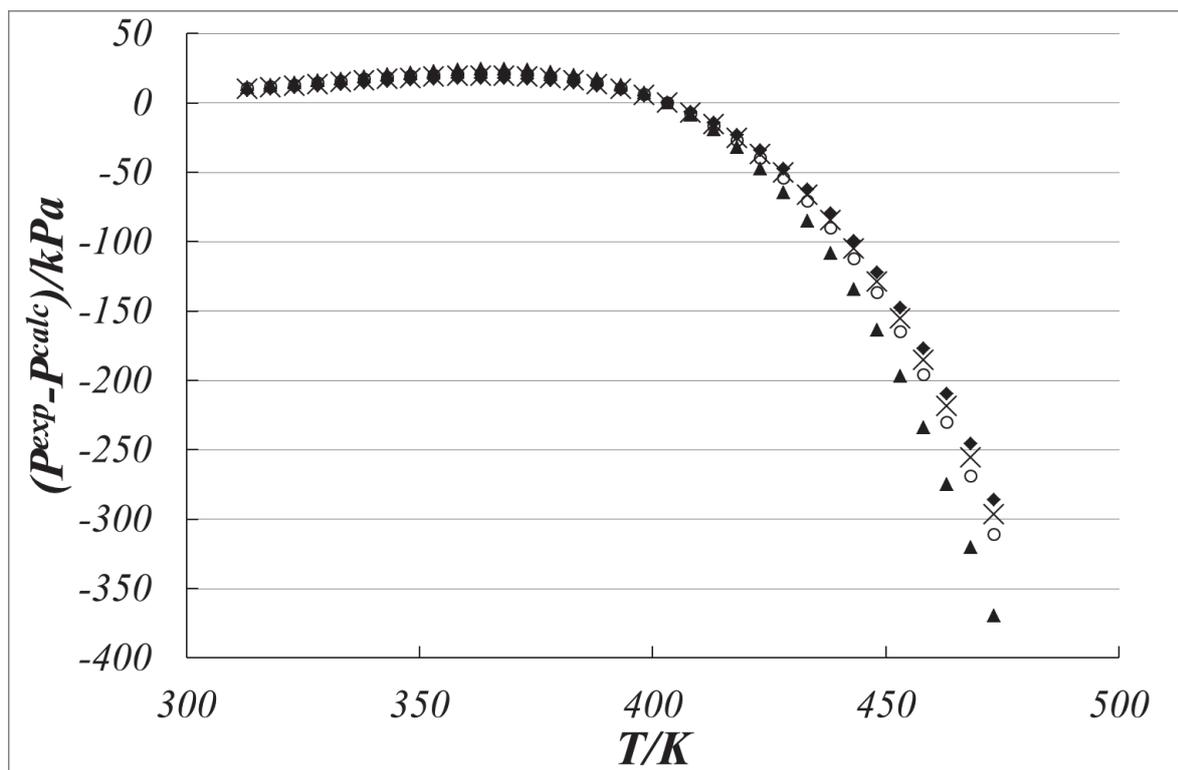


Figure A1 Residuals for different prediction methods using critical data estimated by the Ambrose method for the high end normal boiling point for EEDA. Experimental data presented by Cui et al.(2007). The methods are: (♦) Clapeyron, (▲) Thodos-Gomez hydrogen-bonding, (x) Thodos-Gomez polar and (○) Lee-Kesler.