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Georgios K. Folas

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Ph.D. Thesis

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TECHNICAL UNIVERSITY OF DENMARK
DEPARTMENT OF CHEMICAL ENGINEERING

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Ph.D. Thesis

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Στην αγαπημένη μου γυναίκα Αθανασία,
για την μεγάλη αγάπη της και την συμπαράσταση που μου έδειξε.

To my beloved wife Athanasia,
for her enormous love and support.

ΙΘΑΚΗ

Σα βγεις στον πηγαιμό για την Ιθάκη,
να εύχεσαι νάναι μακρύς ο δρόμος,
γεμάτος περιπέτειες, γεμάτος γνώσεις.
Τους Λαιστρυγόνας και τους Κύκλωπας,
τον θυμωμένο Ποσειδώνα μη φοβάσαι,
τέτοια στον δρόμο σου ποτέ σου δεν θα βρείς,
αν μέν' η σκέψις σου υψηλή, αν εκλεκτή
συγκίνησις το πνεύμα και το σώμα σου αγγίζει.
Τους Λαιστρυγόνας και τους Κύκλωπας,
τον άγριο Ποσειδώνα δεν θα συναντήσεις,
αν δεν τους κουβανείς μες στην ψυχή σου,
αν η ψυχή σου δεν τους στήνει εμπρός σου.

Να εύχεσαι νάναι μακρύς ο δρόμος.
Πολλά τα καλοκαιρινά πρωϊά να είναι
που με τι ευχαρίστησι, με τι χαρά
θα μπαίνεις σε λιμένας πρωτοειδωμένους·
να σταματήσεις σ' εμπορεία Φοινικικά,
και τες καλές πραγμάτειες ν' αποκτήσεις,
σεντέφια και κοράλλια, κεχριμπάρια κ' έβενους,
και ηδονικά μυρωδικά κάθε λογής,
όσο μπορείς πιο άφθονα ηδονικά μυρωδικά·
σε πόλεις Αιγυπτιακές πολλές να πας,
να μάθεις και να μάθεις απ' τους σπουδασμένους.

Πάντα στον νου σου νάχεις την Ιθάκη.
Το φθάσιμον εκεί είν' ο προορισμός σου.
Αλλά μη βιάζεις το ταξίδι διόλου.
Καλλίτερα χρόνια πολλά να διαρκέσει·
και γέρος πια ν' αράξεις στο νησί,
πλούσιος με όσα κέρδισες στον δρόμο,
μη προσδοκώντας πλούτη να σε δώσει η Ιθάκη.

Η Ιθάκη σ' έδωσε το ωραίο ταξίδι.
Χωρίς αυτήν δεν θάβγαινες στον δρόμο.
Αλλο δεν έχει να σε δώσει πια.

Κι αν πτωχική την βρεις, η Ιθάκη δεν σε γέλασε.
Ετσι σοφός που έγινες, με τόση πείρα,
ήδη θα το κατάλαβες η Ιθάκες τι σημαίνουν.

Κωνσταντίνος Π. Καβάφης (1911)

ITHACA

When you set out on your way to Ithaca,
hope that your journey is a long one,
full of adventure, full of knowledge.
The Lestrygonians and the Cyclops,
the angry Poseidon -- do not fear them,
you will never find such as these on your path,
if your thoughts remain lofty, if a fine
emotion touches your spirit and your body.
The Lestrygonians and the Cyclops,
the furious Poseidon you will never encounter,
if you do not carry them within your soul,
if your soul does not set them up before you.

Hope that the journey is a long one.
Many will be the summer mornings
when with such pleasure, with such joy
you will enter ports seen for the first time;
stop at Phoenician markets,
and acquire fine merchandise,
mother-of-pearl and coral, amber and ebony,
and sensual perfumes of all kinds,
as many sensual perfumes as you can;
visit many Egyptian cities,
to learn and learn from scholars.

Always bear Ithaca in your mind.
Arriving there is your ultimate goal.
But do not hurry the voyage at all.
Better to let it last for many years;
and to anchor at the island when you are old,
rich with all you have gained on the way,
not expecting that Ithaca will give you riches.

Ithaca has given you the beautiful journey.
Without her you would have never set out on the road.
She has nothing more to give you.

And if you find her poor, Ithaca has not deceived you.
Wise as you have become, with so much experience,
you must already have understood what Ithacas mean.

C. P. Kavafis (1911)

Preface

This thesis is submitted for the partial fulfillment of the requirements for the Ph.D. degree at the Technical University of Denmark. This work was carried out at the Centre of Phase Equilibria and Separation Processes (IVC-SEP), Department of Chemical Engineering at the Technical University of Denmark, from May 2003 to September 2006, and was funded by STATOIL. The experimental work was carried out in the Research and Development Centre of STATOIL in Trondheim, Norway. My main supervisor was Ass. Prof. Georgios M. Kontogeorgis and co-supervisors were Prof. Erling H. Stenby and Prof. Michael L. Michelsen.

I would like to thank Erling Stenby for giving me the opportunity to work at IVC-SEP. Special thanks to Georgios Kontogeorgis for being always willing to devote time on productive discussions as well as for his excellent guidance during these years. I am also grateful to Michael L. Michelsen for his suggestions and comments which significantly improved the context of this work. Both of them have been a great inspiration for me and I honestly enjoyed working with them.

My thanks to my co-workers at the Statoil Research Centre who helped me with the experimental part of this work. Thanks to Toril Haugum and Andreas Bruås who introduced me to GC analysis and to the experimental procedure for the measurements. I especially need to thank Dr. Even Solbraa for our excellent collaboration during this project. I wish to acknowledge STATOIL (Trondheim) for the financial support of this work and for giving permission to publish all the experiment results I obtained during my stay in Trondheim. Thanks to Morten Rode Kristensen for being willing to translate the summary of the thesis in Danish.

Finally I would like to thank some people who contributed positively to my Ph.D. studies in one way or another. I would like to thank my family and especially my wife, Athanasia, for being always patient and understanding with me and my friend Vasilis Inglezakis for changing my point of view of research.

Kongens Lyngby, September 2006

Georgios Konstantinou Folas

Contents

Summary

Our purpose in this thesis is two-fold: First to test the applicability of thermodynamic models which are capable of handling polar/associating fluids to different types of phase equilibria and second to perform new experimental measurements for systems of interest to the gas/oil industry in cases where literature data are scarce. The thesis, after a short introduction, is divided into the following chapters:

Chapter 1 presents a description of the thermodynamic models considered in this work.

Chapter 2 presents the applicability of the Cubic-Plus-Association (CPA) EoS, which is a model that explicitly account for hydrogen bonding via an association term (the same as in SAFT model), to binary mixtures of water – alcohols or water – glycols. Different types of phase equilibria (VLE, LLE and SLE) are considered while an effort is put on using only temperature independent binary interaction parameters (k_{12}) over extensive temperature or pressure ranges. Some limitations related to the association term are identified.

Chapter 3 provides a study of the associating sites for water and alcohols within the CPA framework in an effort to understand and hopefully solve some of the limitations of the model in mixtures with water. The association scheme of water is investigated and it is found that the 4-site molecule is the optimum choice for CPA. A 3-site scheme is investigated for alcohols (in parallel to the previously established 2-site scheme), which is in accordance to their chemical structure. The performance of the two schemes for VLE, LLE and SLE calculations of alcohol – hydrocarbon binary mixtures is evaluated, both at low and high pressures. Phase equilibria calculations for the solvating water – alcohols mixtures and multicomponent prediction results with both schemes are evaluated. It is concluded that the 2-site scheme for alcohols in the best for CPA.

The study of binary and multicomponent systems containing aromatic hydrocarbons is presented in chapters 4 to 6. Chapter 4 presents results of the extension of CPA to binary systems containing water/alcohol – aromatic hydrocarbons and calculations of multicomponent systems in the presence of aromatic components. A way to account for the solvation between an associating component and an aromatic hydrocarbon is presented in this chapter, which is found to provide satisfactory results.

Chapter 5 presents new experimental LLE measurements for glycol – aromatic hydrocarbon systems and mixtures with water as a third component. The systems studied are ethylene glycol

(MEG) – benzene/toluene, triethylene glycol (TEG) – benzene/toluene, MEG – water – benzene, MEG – water – toluene and TEG – water – toluene. The systems are correlated or predicted (for the ternary ones) with CPA and the results are compared to an industrial simulator.

Chapter 6 presents LLE calculations using SRK EoS with G^E mixing rules, which is a conventional engineering method to account for polar/associating mixtures and previously shown to provide satisfactory results for methanol related systems. Calculations are performed for water/glycol – hydrocarbons (both aliphatics and aromatics) and compared to CPA. The predictive performance of both models is further evaluated in multicomponent multiphase equilibria of mixtures containing ethylene glycol as a gas hydrate inhibitor.

Chapter 7 presents some applications of CPA to mixtures containing acetone or dimethyl ether. An alternative approach for modeling systems containing acetone is presented, where acetone is assumed to be a self associating compound.

Chapter 8 presents gas phase water content predictions with CPA (using no binary interaction parameter) for water – methane, water – nitrogen and natural gas mixtures and a comparison of the ISO standard (GERG) model. When the gas phase is in equilibrium with a heavy phase other than liquid (i.e. hydrate or ice) CPA is combined with a suitable solid phase model. The method is found to provide similar and occasionally better results to GERG model.

Chapter 9 is a brief presentation of the main conclusions that have been derived from the present work as well as preliminary results/suggestions that might be considered as future challenges.

Dansk Resumé

Formålet med denne afhandling er dels at teste anvendeligheden af termodynamiske modeller, der kan håndtere polære/associerende fluider, på forskellige typer faseligevægte, samt dels at foretage nye eksperimentelle målinger på systemer af interesse for olie- og gasindustrien, hvor der er mangel på data i litteraturen. Efter en kort introduktion er afhandlingen inddelt i følgende kapitler:

Kapitel 1 giver en beskrivelse af de termodynamiske modeller, som anvendes i dette arbejde.

Kapitel 2 viser anvendelsen af Cubic–Plus–Association (CPA) tilstandsmodellen på binære blandinger af vand-alkohol og vand-glykol. CPA modellen er en model, der eksplicit tager højde for hydrogenbindinger via et associationsled (tilsvarende SAFT modellen). Forskellige typer faseligevægte (gas-væske (VLE), væske-væske (LLE) og faststof-væske (SLE)) er undersøgt, hvor der er lagt vægt på kun at benytte temperaturuafhængige binære interaktionsparametre (k_{12}) over store tryk- og temperaturintervaller. Visse begrænsninger relateret til associationsleddet er identificeret.

I kapitel 3 studeres associationspositionerne for vand og alkoholer inden for rammen af CPA modellen i bestræbelse på at forstå og forhåbentligt løse nogle af modellens begrænsninger, når den anvendes på blandinger indeholdende vand. Associationsskemaet for vand er således undersøgt, og resultaterne viser, at et molekyle med 4 bindingspositioner er optimalt i CPA modellen. Et skema med 3 bindingspositioner er undersøgt for alkoholer (parallelt med det tidligere etablerede skema med 2 bindingspositioner), hvilket er i overensstemmelse med deres kemiske struktur. De to skemaer er evalueret ved VLE, LLE og SLE beregninger for binære vand – kulbrinte blandinger ved både lavt og højt tryk. Faseligevægtsberegninger for associerende vand-alkohol blandinger samt resultater af prædiktioner i flerkomponent blandinger er ligeledes evalueret. Det konkluderes, at skemaet med 2 bindingspositioner for alkoholer er bedst for CPA modellen.

I kapitel 4 til 6 præsenteres studier af binære og flerkomponent systemer indeholdende aromatiske kulbrinter. Kapitel 4 viser resultater fra udvidelsen af CPA modellen til binære systemer bestående af vand/alkohol – aromatiske kulbrinter samt beregninger på flerkomponent systemer indeholdende aromatiske forbindelser. I dette kapitel præsenteres ligeledes en metode, som har vist tilfredsstillende resultater, til håndtering af krydsassociationen mellem en associerende komponent og en aromatisk kulbrinte.

Kapitel 5 præsenterer nye eksperimentelle LLE målinger for glykol – aromatisk kulbrinte blandinger med vand som tredje komponent. Følgende systemer er undersøgt: ethylen glykol (MEG) – benzen/toluen, triethylen glykol (TEG) – benzen/toluen, MEG – vand – benzen, MEG – vand – toluen samt TEG – vand – toluen. Systemerne er enten korrelerede eller prædikterede (for de ternære systemer) med CPA modellen, og resultaterne er sammenlignet med resultater fra en industriel simulator.

I kapitel 6 præsenteres LLE beregninger med SRK tilstandsligningen og G^E blandingsregler, som er den konventionelle metode til håndtering af polære/associerende blandinger, og som tidligere har vist tilfredsstillende resultater for methanol systemer. Der er foretaget beregninger for vand/glykol – kulbrinte (både alifatiske og aromatiske) blandinger, som er sammenlignet med CPA modellen. De prædiktive egenskaber for begge modeller er yderligere undersøgt i flerkomponent flerfase ligevægte for blandinger indeholdende ethylen glykol som gashydrat inhibitor.

Kapitel 7 giver eksempler på anvendelse af CPA modellen på blandinger indeholdende acetone eller dimethyl ether. En alternativ tilgang til modellering af acetone præsenteres, hvor acetone betragtes som en selv-associerende komponent.

Kapitel 8 præsenterer prædiktioner af gasfase vandindholdet med CPA modellen (uden brug af binær interaktionsparameter) for vand – methan, vand – nitrogen samt naturgas blandinger. Resultaterne er sammenlignet med ISO standard (GERG) modellen. For tilfælde, hvor en gasfase er i ligevægt med en tung fase, der ikke er væske (f.eks. hydrat eller is), kombineres CPA modellen med en passende model for den faste fase. Denne metode giver tilsvarende, og i visse tilfælde bedre, resultater end GERG modellen.

I kapitel 9 gives slutteligt en kort præsentation af afhandlingens hovedkonklusioner sammen med foreløbige resultater/forslag, der kan betragtes som fremtidige udfordringer.

Introduction

During transportation and further processing of natural gas inhibitors are continuously added to the mixture in order to prevent the formation of gas hydrates. Typical chemicals that are used as hydrate inhibitors are ethylene glycol (MEG) and methanol. The trend towards long distance multiphase flow pipelines, which are based on the sea bottom, increases the need for accurate calculations of mixtures containing water, an inhibitor, a gas phase and a condense phase. In the Hammerfest LNG plan in Norway for example, monoethylene glycol (MEG) is transferred in its own pipeline from the land and gets injected offshore into the wellstream at the choke, in order to inhibit the formation of gas hydrates. The mixture, containing natural gas, water, MEG and condensate is transferred onshore to Snøvit through a 143 km long pipeline. At the beginning of the pipeline, the mixture has a pressure of 130bar and a temperature of about 25^{o}C which is within the temperature range that hydrates can form. During the journey to land, the mixture will decline in temperature to 4 – 5 ^{o}C and pressure of 70 – 90bar when reaching the landward end. The three phases are separated onshore and sent to further treatment. In the transportation process MEG is lost in the vapor phase as well as in the condensate phase; it is therefore desired to accurately predict the distribution of MEG in the three phases.

Another application where such chemicals are of importance is during the further processing of gas, where glycols and mainly tri-ethylene glycol (TEG) is commonly used for removing the water. This is because free water in a natural gas stream can result in line plugging due to hydrate formation, reduction of line capacity due to collection of free water in the line, and increased risk of damage to the pipeline due to the corrosive effects of water. Reducing the water vapor content of natural gas reduces its saturation temperature (or dew point) means reducing the chance that free water will form in the pipeline. Hence, major transportation pipelines usually impose restrictions on the water content of the natural gas that is allowed into the pipeline. Glycol dehydration is an absorption dehydration process, where glycol, when in contact with a stream of natural gas that contains water, will serve to 'steal' the water out of the gas stream.

For optimizing such processes there are several operational challenges related to the water / hydrocarbon / glycol (methanol) phase behavior, such as i) accurate calculation of the loss of glycol (methanol) in the gas and condensate phase, ii) prediction of hydrate formation in hydrocarbon / water/glycol (methanol) solutions, iii) freezing (ice/MEG) of hydrocarbon / water / glycol solutions. The purpose of this Ph.D. project, initiated by STATOIL, is to contribute to the understanding and possibly provide some improvements in order to enable operations of the pipelines and processing plans in an optimal way. The Cubic-Plus-Association (CPA) Equation of State (EoS) is chosen as the main engineering tool to be tested for the following reasons: i) the model was previously shown to correlate satisfactory LLE of water – hydrocarbon systems ii) successful LLE results of glycols – HC's and methanol – HC's systems were obtained, iii) satisfactory VLE results of glycols (methanol) – water binary systems were achieved and iii) the model reduces to the classical SRK EoS (with parameters fitted to vapor pressure and liquid density data) for applications with hydrocarbons.

In order to contribute to the understanding of the phase behavior of such systems experimental measurements were also performed for systems containing glycols, water and aromatic hydrocarbons because aromatic hydrocarbons are also present in the natural gas, thus in lower concentrations as the aliphatic ones. Finally the performance of the CPA model was also compared to conventional engineering models in an effort to identify improvements and limitations.

Chapter 1.

Thermodynamic Models Description

1.1. Introduction

Modeling of phase equilibria of complex mixtures containing hydrogen bonding components is a challenging issue in the area of thermodynamics. It is well known that classical cubic EoS (i.e. SRK or PR) often fail to correlate the phase equilibria of such systems, due to the strong hydrogen bonding forces which cannot be well captured by the attractive term of such EoS, especially when van der Waals one fluid mixing rules are used. The ability, however, of EoS to perform phase equilibria calculations both at low and high pressures lead to the idea of combining EoS with excess Gibbs energy models, resulting to the so-called EoS/G^E models. These models were shown to provide satisfactory results for highly solvating systems at various temperatures and pressures, as for example the binary methanol – water or ethanol – water systems using SRK and MVH2 mixing rule[1] with modified UNIFAC as an activity coefficient model. The classical SRK[2] EoS performs adequate only for some of them at specific conditions.

Over the last decade, substantial progress has been made regarding the development of thermodynamic models which can successfully perform phase equilibrium calculations for highly solvating systems. The essence of this progress is to use statistical mechanical methods, such as Wertheim's first order perturbation theory[3-6]. Wertheim, using perturbation theory with a potential function that mimics hydrogen bonding, developed a statistical mechanical model for systems with a repulsive core and multiple hydrogen bonding sites. A combination of this theory with existing thermodynamic models results in models which could in principle explicitly account for solvation. Such a model is the CPA EoS which is presented in section 1.2. Although the thesis focuses on modeling associating systems with the CPA EoS, selected EoS/G^E models which were found successful for such applications are also used for comparison purposes. This chapter presents a description of the thermodynamic models used in the thesis.

1.2. The CPA Equation of State – model description

The Cubic-Plus-Association (CPA) model is an equation of state that combines the simplicity of a cubic equation of state (the Soave-Redlich-Kwong[2], SRK) and the association term derived from Wertheim's theory[3-6], as in SAFT. The SRK model accounts for the physical interactions between the molecules. The association term takes into account the specific site-site interaction due to hydrogen bonding between like molecules (self-association) and unlike molecules (cross-association or solvation). Dipolar and quadrupolar interactions are not explicitly accounted for.

Since the association term is based on Wertheim's first-order thermodynamic perturbation theory (TPT-1), in the engineering framework introduced by Chapman et al.[7,8], the assumptions inherent in the SAFT approach also apply to CPA. In particular, the activity of each bonding site is assumed independent of the other bonding sites on the same molecule. Therefore, steric hindrance effects are neglected. Furthermore, no site on the same molecule can bond simultaneously to two different sites on another molecule, and finally double bonding between molecules is not allowed. Hence, ring-like bonding structures are neglected and only tree-like formations are included. It is however of interest to mention that Wertheim has extending his theory in order to deal with ring – like structures[9] and has shown that by extended the thermodynamic perturbation theory to second order[10], the theory can account for cases in which hydrogen bonding at one site prevents bonding at another. However, CPA is based on the first order thermodynamic perturbation theory.

The CPA equation of state can be expressed in terms of pressure as a sum of the SRK equation of state and the contribution of association term as given by Michelsen and Hendriks[11]:

$$P = \frac{RT}{V_m - b} - \frac{\alpha(T)}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \frac{1}{V_m}\frac{\partial \ln g}{\partial(1/V_m)}\right)\sum_i x_i \sum_{A_i}(1 - X_{A_i}) \tag{1.1}$$

where V_m is the molar volume, X_{A_i} is the fraction of A-sites on molecule i that do not form bonds with other active sites, and x_i is the mole fraction of component i. The letters i and j are used to index the molecules while A and B indicate the bonding sites on a given molecule.

In equation (1.1) the association term is in the form derived by Michelsen and Hendriks[11]. It is identical to the original expression (Chapman et al.[7,8], Huang and Radosz[12], Kontogeorgis et al.[13]) which employs the derivatives of X_{A_i} with respect to molar density but much simpler, thus substantially simplifying and speeding-up the calculations, in particular when derivatives are needed.

X_{A_i}, which is the key property in the association term, satisfies the following set of equations

$$X_{A_i} = \frac{1}{1 + \frac{1}{V_m}\sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \tag{1.2}$$

where B_j indicates summation over all sites.

$\Delta^{A_iB_j}$, the association (binding) strength between site A on molecule i and site B on molecule j is given by

$$\Delta^{A_iB_j} = g(V_m)^{ref}\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right)-1\right]b_{ij}\beta^{A_iB_j} \tag{1.3}$$

$\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ are the association energy and volume of interaction between site A of molecule i and site B of molecule j, respectively, and $g(V_m)^{ref}$ is the radial distribution function for the reference fluid (i.e. fluid of hard spheres).

Originally, in CPA EoS as presented by Kontogeorgis et al.[13] the radial distribution function derived from the Carnahan – Starling equation of state was used[14], which is given by

$$g(V_m)^{ref} = \frac{2-\eta}{2(1-\eta)^3} \tag{1.4}$$

with $\eta = \frac{1}{4V_m}b$ (1.5)

where η is the reduced fluid density.

The use of the Carnahan - Starling radial distribution function is an approximation since CPA employs the van der Waals repulsive term of SRK and not the more rigorous Carnahan-Starling term for the hard-sphere fluid as in SAFT.

Kontogeorgis et al.[15] proposed a simpler expression for g (sCPA):

$$g(V_m)^{ref} = \frac{1}{1-1.9\eta}, \text{ with } \eta = \frac{1}{4V_m}b \tag{1.6}$$

All phase equilibria calculations performed in this work are based on the simplified CPA model (referred to as sCPA) employing the simplified radial distribution function, equation (1.6).

1.2.1. Parameters for pure compounds

The energy parameter $\alpha(T)$ in the SRK part (eq. 1.1) is given by a Soave-type temperature dependency:

$$\alpha(T) = a_o(1+c_1(1-\sqrt{T_r}))^2 \tag{1.7}$$

T_r is the reduced temperature (T/T_c) of the component i.

CPA has five pure-compound parameters; three for non-associating compounds (a_0, b, c_1) and two additional parameters for associating compounds($\varepsilon^{A_iB_i}$, $\beta^{A_iB_i}$). The five pure-compound parameters are usually obtained by fitting experimental vapor pressure and saturated liquid density data. For non-associating compounds, the three parameters can either be obtained by fitting vapor pressure and liquid density data or in the conventional way from critical temperatures, pressures and the acentric factor.

If one wishes to apply the conventional way for estimating the energy and the co – volume parameters of the SRK EoS for a component i (since for non – associating components the model reduces to the classical SRK EoS), then the classical expressions are required:

$$\begin{aligned} \alpha(T) &= 0.42748\frac{R^2T_C^2}{P_C}\left[1+c_1(1-\sqrt{T_r})\right]^2 \\ c_1 &= 0.48+1.574\omega-0.176\omega^2 \\ b &= 0.08664\frac{RT_C}{P_C} \end{aligned} \tag{1.8}$$

Use of CPA together with equation (1.7) requires knowledge of the experimental critical temperature which has been used in the parameter estimation and is required for phase equilibrium calculations. This procedure may be somewhat inconvenient as it requires that the experimental critical temperature (T_c) used in the calculations is also reported. Thus an alternative approach which eliminates the need to know the critical temperature is presented in Appendix B.

1.2.2. Mixing rules

The extension of the CPA EoS to mixtures requires mixing rules only for the parameters of the SRK-part. The mixing and combining rules for $\alpha(T)$ and b are the classical van der Waals one-fluid ones:

$$\alpha(T) = \sum_i\sum_j x_ix_j\alpha_{ij} \tag{1.9}$$

$$b = \sum_i\sum_j x_ix_jb_{ij} \tag{1.10}$$

where the classical combining rules are used:

$$\alpha_{ij} = \sqrt{\alpha_i\alpha_j}(1-k_{ij}) \tag{1.11}$$

$$b_{ij} = \frac{b_i+b_j}{2} \tag{1.12}$$

1.2.3. Cross-associating systems

Combining rules for the association energy and volume parameters are needed between different associating molecules, i.e. $i \neq j$ e.g. water-alcohol or water-glycol systems, in order to calculate the value of the association strength in equation (1.3). Over the last years various combining rules have been investigated[16,17]; those are summarized in table 1.1.

As recently shown by Derawi et al.[16] for the CR-1 combining rule, the arithmetic mean for the cross-association energy is proportional to the enthalpy of hydrogen bonding (ΔH_{12}) and the geometric mean for the cross-association volume is also related to the cross-entropy of the hydrogen bonding. Equivalent theoretical justifications can be obtained for ECR (see equation 1.14), because both combining rules are functionally similar as shown below. The other combining rules seem to lack theoretical explanation.

From previous investigations[16,17] and the results presented in this thesis, two choices have been identified as very successful in various cases, the so-called CR-1 rule:

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \qquad \beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}} \tag{1.13}$$

or alternatively, the so-called Elliott combining rule (ECR)[32]:

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}} \tag{1.14}$$

The CR-1 and ECR rules are functionally similar; the only difference is the function of b in the expression for the cross – association volume (which is important for size-asymmetric systems e.g. water with heavy alcohols or glycols).

Assuming that the term $\exp(\frac{\varepsilon^{AB}}{RT}) >> 1$ it can be shown that the equivalent expressions for the cross – association energy and cross – association volume parameters with ECR are:

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \text{ and } \beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}}\,\frac{\sqrt{b_ib_j}}{b_{ij}} \tag{1.15}$$

In chapter 4 the CPA EoS is extended to binary water-aromatic hydrocarbon systems, and further in chapter 5, systems containing glycols and aromatic hydrocarbons are considered. Even though aromatics do not self-associate, they can interact with an associating compound, such as water. To account for solvation a modified CR-1 combining rule is suggested (mCR-1), allowing however the cross association volume $\beta^{A_iB_j}$ (or *BETCR*) to be determined from the experimental data. Thus, the cross-association energy parameter for associating-aromatic or olefinic mixtures is equal to the value of the associating compound (water, alcohol or glycol) divided by two:

$$\varepsilon^{A_iB_j} = \frac{\varepsilon_{associating}}{2} \tag{1.16}$$

and $\beta^{A_iB_j} = BETCR$ (fitted) (1.17)

Then, the association strength will be estimated by equation (1.3) and in this way the in-built temperature dependency of the cross-association strength is retained for solvating systems. The calculations presented in chapters 4 and 5 have showed that this approach provides satisfactory results over extended temperature ranges.

Table 1.1. Proposed combining rules for the cross – association energy and volume in the association term of CPA EoS.

combining rule	**cross – association energy** ($\varepsilon^{A_iB_j}$)	**cross – association volume** ($\beta^{A_iB_j}$)
CR-1	$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2}$	$\beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}}$
CR-2	$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2}$	$\beta^{A_iB_j} = \frac{\beta^{A_iB_i} + \beta^{A_jB_j}}{2}$
CR-3	$\varepsilon^{A_iB_j} = \sqrt{\varepsilon^{A_iB_i}\varepsilon^{A_jB_j}}$	$\beta^{A_iB_j} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}}$
CR-4	$\varepsilon^{A_iB_j} = \sqrt{\varepsilon^{A_iB_i}\varepsilon^{A_jB_j}}$	$\beta^{A_iB_j} = \frac{\beta^{A_iB_i} + \beta^{A_jB_j}}{2}$
cross – association (binding) strength		
Elliott rule (ECR)	$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}}$	

1.2.4. Association sites and monomer fraction

As seen in equation (1.2), the association term of CPA depends on the choice of the association scheme i.e. number and type of association sites for the associating compound. Huang and Radosz[12] have classified eight different association schemes and the terminology of their manuscript is also used here. Table 1.2 provides a schematic explanation of the association schemes referred in the thesis, which are based on the terminology of Huang and Radosz[12].

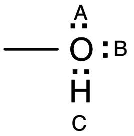
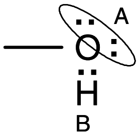
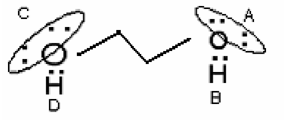
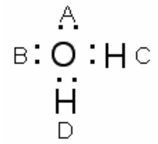
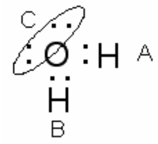
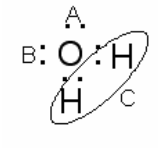
Different molecules are characterized by different schemes and various possibilities are investigated: in chapter 3 the two-site (2B) and three-site (3B) association scheme are investigated for alcohols. In the 3B formalism, sites A and B correspond to oxygen lone pairs, while site C corresponds to a hydrogen atom. Due to the asymmetry of the association, the fraction of non-bonded hydrogen atoms (X^C) is not equal to the fraction of non-bonded lone pairs (X^A or X^B). In the 2B formalism, the two lone-pair oxygens are considered to be a single site.

The four-site (4C) association scheme is used in this work for glycols in accordance to Derawi et al.[16, 18]. The 4C scheme (four association sites) has two proton donors and two proton acceptors per molecule. Although glycols have at least 6 sites based on their chemical structure, the choice of the 4C association scheme is consistent to the 2B scheme for alcohols, where the two lone-pair oxygens are considered to be a single site.

The four site (4C) association scheme is traditionally used for water[15-17,23] within the CPA framework. In the case of water in the 4C formalism, the bonding symmetry means that all non-bonded site fractions are equal. In chapter 3, however, a short investigation of the association scheme of water is presented, since water is a key component in the majority of systems studied in this work. In the 3B formalism, either the two-lone pair electrons on the oxygen atom are considered to be a single site, or else (and of course less likely from the physical point of view) the two hydrogen atoms are lumped together into a single site – labeled C.

In all cases, the fraction of monomers (completely non-bonded molecules, X_1) is equal to the product of the fractions of all non-bonded site types. In cases where bonding is symmetrical (2B and 4C), the fraction of non-bonded sites is assumed to be equal for all types of site.

Table 1.2. Association schemes based on the terminology of Huang and Radosz[12].

Species	**Formula**	**Type**	**Site fractions (X)**
Alcohol		3B	$X^A = X^B;\ X^C = 2X^A - 1$ $X_1 = X^A X^B X^C$
		2B	$X^A = X^B$ $X_1 = X^A X^B$
Glycols		4C	$X^A = X^B = X^C = X^D$ $X_1 = X^A X^B X^C X^D$
Water		4C	$X^A = X^B = X^C = X^D$ $X_1 = X^A X^B X^C X^D$
		3B	$X^A = X^B;\ X^C = 2X^A - 1$ $X_1 = X^A X^B X^C$
		3B	$X^A = X^B;\ X^C = 2X^A - 1$ $X_1 = X^A X^B X^C$

1.2.5. List of CPA pure compound parameters

After the brief explanation of the various association schemes, this section presents the suggested CPA pure compound parameters for the components involved in this work. The CPA parameters for inert components as summarized in table 1.3, while table 1.4 presents the CPA parameters for the associating components. The 2B association scheme is used for alcohols and the 4C scheme for water, since, as will be presented in chapter 3, those are concluded to perform best; glycols are assumed to be 4C molecules, according to Derawi et al.[16,18]. All parameters are presented in the conventional form together with the experimental critical temperature used for the calculations, because this form is used in all CPA publications so far.

Table 1.3. CPA parameters for the inert compounds considered in this work.

Component	**Ref**	a_0 **(bar l^2 mol^{-2})**	b **(l/mol)**	c_1	T_c **(K)**	**ΔP** (%)	**Δρ** (%)
propane	20	9.118	0.05783	0.6307	369.83	0.9	1.9
butane	20	13.143	0.07208	0.7077	425.18	0.2	1.0
iso-butane	21	12.909	0.07470	0.7021	408.14	0.5	0.6
n-pentane	20	18.198	0.09101	0.7986	469.70	0.5	0.9
n-hexane	20	23.681	0.10789	0.8313	507.60	0.5	0.5
cyclohexane	20	21.257	0.09038	0.7427	553.58	0.4	1.1
n-heptane	20	29.178	0.12535	0.9137	540.20	0.3	0.5
n-octane	20	34.875	0.14244	0.9942	568.70	0.4	0.6
iso-octane	22	32.141	0.13875	0.8699	543.96	0.2	1.0
n-nonane	this work	41.251	0.16035	1.0463	594.60	0.3	0.7
n-decane	20	47.389	0.17865	1.1324	617.70	0.4	0.6
n-undecane	this work	55.220	0.19791	1.1437	639.00	0.6	0.9
n-dodecane	23	62.403	0.21624	1.1953	658.00	1.1	1.0
n-tetradecane	22	76.618	0.25053	1.2906	693.00	0.9	0.8
n-pentadecane	this work	85.637	0.27453	1.3404	708.00	0.3	1.4
n-hexadecane	22	94.914	0.29610	1.3728	723.00	0.4	1.8
n-octadecane	this work	110.810	0.33369	1.4698	747.00	0.3	1.6
n-nonadecane	this work	119.724	0.35389	1.5084	758.00	0.6	1.8
n-eicosane	this work	129.530	0.37438	1.5367	768.00	0.6	2.0
benzene	20	17.876	0.07499	0.7576	562.16	0.9	1.0
toluene	20	23.375	0.09214	0.8037	591.80	0.2	0.6
ethylbenzene	this work	28.860	0.10872	0.8539	617.20	0.2	0.4
propylbenzene	this work	34.821	0.12685	0.9117	638.38	0.1	0.4
butylbenzene	this work	41.294	0.14440	0.9618	660.55	0.3	0.5
pentylbenzene	this work	48.415	0.16167	0.9795	679.90	1.1	0.5
hexylbenzene	this work	55.3223	0.18022	1.0436	698.00	0.9	0.7
m-xylene	this work	29.086	0.10872	0.8681	617.05	0.1	0.7
1-hexene	23	21.983	0.10200	0.8430	504.03	0.7	1.2
1-octene	23	33.630	0.13780	0.9700	566.60	1.2	1.0
1-decene	this work	46.579	0.17333	1.0642	616.40	0.5	0.5

Table 1.4. CPA parameters for the associating compounds considered in this work.

Compound	**Ref**	a_0 **(bar l^2 mol^{-2})**	b **(l/mol)**	c_1	**ε^{AB} (bar l mol^{-1})**	**β^{AB}*10^3**	T_c **(K)**	**ΔP (%)**	**Δρ (%)**
water	15	1.228	0.01452	0.6736	166.55	69.2	647.29	0.8	0.5
methanol	15	4.053	0.03098	0.4310	245.91	16.1	512.64	0.6	0.5
ethanol	this work	8.672	0.04908	0.7369	215.32	8.0	513.92	1.3	0.3
propanol	this work	11.910	0.06413	0.9171	210.01	8.1	536.78	0.4	0.5
iso-propanol	this work	10.602	0.06410	0.9468	210.01	9.1	508.30	0.2	0.4
1-butanol	this work	15.695	0.07970	0.9784	210.01	8.2	563.05	0.9	1.0
1-pentanol	this work	22.758	0.09746	0.9358	210.01	3.6	586.15	0.2	0.5
1-octanol	this work	41.582	0.14845	1.1486	267.59	0.14	652.50	0.8	0.5
1-dodecanol	this work	71.756	0.22137	0.9650	337.91	0.12	719.40	1.4	0.7
MEG	24	10.819	0.05140	0.6744	197.52	14.1	720.00	0.9	1.6
DEG	24	26.408	0.09210	0.7991	196.84	6.4	744.60	1.8	1.6
TEG	24	39.126	0.13210	1.1692	143.37	18.8	769.50	3.0	1.6

1.3. The SRK/HV Equation of State with modified NRTL

The concept of EoS / G^E is to combine the advantages of cubic EoS with activity coefficient models in order to have a model valid both at high pressures and for polar compounds that exhibit high deviations from ideality in the liquid phase. Huron and Vidal[19] were the first to combine equations of state with excess Gibbs energy models, by matching the excess Gibbs energy from the EoS to that of an activity coefficient model at infinite pressure, and solving for the van der Waals attractive parameter ($\alpha(T)$):

$$\left(\frac{G^E}{RT}\right)_P^{EoS} = \left(\frac{G^E}{RT}\right)_P^{\mathrm{mod}el,*} \tag{1.18}$$

The superscript * refers to the specific activity coefficient model used e.g. NRTL. The equality should then be valid at a specific (fixed) pressure, called the "reference pressure" e.g. infinite or zero pressure. Then by solving this equality with respect to the energy parameters of the EoS the resulting mixing rule will include the activity coefficient model.

Huron and Vidal used the infinite reference pressure. Their argument is that if G^E at infinite pressure has a finite value the volume at infinite pressure must be identical to the co–volume of the molecule (the b parameter in SRK EoS). In this way Huron and Vidal obtained a mixing rule for the energy parameter of the equation of state, which is an explicit expression of the excess Gibbs energy model. The SRK/HV model uses the SRK EoS:

$$P = \frac{RT}{V_m - b} - \frac{\alpha(T)}{V_m(V_m + b)} \tag{1.19}$$

The temperature dependence of the energy term $\alpha(T)$, for the component i, is given by the classical expression of the SRK EoS, calculated by the critical pressure, critical temperature and acentric factor, given by equation (1.8). Pedersen et al.[25] used for polar components, such as water or methanol, a Mathias – Copeman[26] expression for the energy parameter of the component i:

$$\begin{gathered}\alpha(T) = 0.42747\frac{R^2T_c^2}{P_c}\left[f(T_r)\right]^2 \\ f(T_r) = 1 + Q_1(1-\sqrt{T_r}) + Q_2(1-\sqrt{T_r})^2 + Q_3(1-\sqrt{T_r})^3\end{gathered} \tag{1.20}$$

1.3.1. Mixing Rules

When extending the model to mixtures, the classical one fluid Van der Waals mixing rule is used for the co-volume parameter given by equation (1.10) and (1.12), while for the energy term the mixing rule suggested by Huron and Vidal, which is an explicit expression of the excess Gibbs energy model is used:

$$\alpha(T) = b\left[\sum_i x_i \frac{\alpha_i}{b_i} - \frac{G_\infty^E}{\ln 2}\right] \tag{1.21}$$

In principle any reasonable model usually based on local composition can be used in equation. (1.21). Huron and Vidal used a modification of the NRTL model:

$$\frac{G_\infty^E}{RT} = \sum_{i=1}^{N} x_i \frac{\sum_{j=1}^{N} \tau_{ji} x_j b_j \exp(-\alpha_{ji}\tau_{ji})}{\sum_{k=1}^{N} x_k b_k \exp(-\alpha_{ki}\tau_{ki})} \tag{1.22}$$

where: $\tau_{ji} = (g_{ji} - g_{ii})/RT$ (1.23)

α_{ij} is a non-randomness parameter taking into account that the mole fraction of molecules of type i around a molecule of type j may deviate from the overall mole fraction of molecules of type i in the mixture, and g_{ji} is an energy parameter characteristic of the $j-i$ interaction.

Huron and Vidal in their original manuscript[19] showed that this specific excess Gibbs energy expression can be parameterized in such a manner that the results of the classical van der Waals mixing rule are exactly reproduced. The specific choice is:

$$\begin{aligned} &\alpha_{ij} = 0 \\ &g_{ii} = -\frac{\alpha_i}{b_i}\ln 2 \\ &g_{ji} = -2\frac{\sqrt{b_i b_j}}{b_i + b_j}\sqrt{g_{ii} g_{jj}}(1-k_{ij}) \end{aligned} \tag{1.24}$$

In this case k_{ij} is the classical SRK binary interaction parameter. The obvious importance of this modification is that the model can be easily used for multicomponent multiphase equilibria using the HV mixing rule for specific cases of binary systems (such as polar components) and the classical SRK for the hydrocarbon binaries.

1.4. The SRK/MHV2 Equation of State with modified UNIFAC of Larsen

The use of the infinite pressure as a reference pressure by Huron and Vidal has the limitation that activity coefficient models such as UNIFAC or NRTL with published low pressure parameters cannot be used directly. This is because available parameters for these activity coefficient models, as for example in DECHEMA database, are estimated at low pressures. Thus, since Huron – Vidal mixing rule is derived at infinite pressure, the parameters have to be refitted.

To make possible the use of activity coefficient model parameters fitted to low pressure data, Mollerup[27] suggested the matching of the excess Gibbs energy model of an EoS to that of an activity coefficient model at zero pressure. The zero pressure approach was further investigated by Michelsen[28,29] and lead, after a modification developed by Dahl and Michelsen[1], to an explicit expression for the mixing rule of the energy term, known as the MHV2 mixing rule. As in the case of SRK/HV EoS, equation (1.19) is also the expression of pressure for SRK/MHV2, while the pure component co-volume and energy parameter are estimated from equation (1.8) similar to SRK/HV. Alternatively a Mathias – Copeman expression can be used to the calculation of the energy parameter of the pure components, given by equation (1.20). As discussed by Dahl and Michelsen[1] this approach provides superior VLE results for binary systems of polar or associating components (i.e. water, alcohols).

1.4.1. Mixing Rules

The classical one fluid Van der Waals mixing rule is used for the co-volume parameter given by equations (1.10) and (1.12), while the mixing rule for energy term is given by the following equation:

$$-0.478(\alpha-\sum_i x_i\alpha_i)-0.0047(\alpha^2-\sum_i x_i\alpha_i^2)=\frac{G^E}{RT}+\sum_i x_i\ln\frac{b}{b_i} \tag{1.25}$$

The larger root of the quadratic equation (1.25) is the value for the energy parameter $\alpha(T)$ which should be used in equation (1.19)

Once again any reasonable activity coefficient model shall be used as an excess Gibbs energy model. In this thesis the modified UNIFAC proposed by Larsen et al.[30] is used. The activity coefficient of a component *i* is calculated as in the original UNIFAC, as the sum of the combinatorial and the residual term:

$$\ln \gamma_i = \ln \gamma_i^{com} + \ln \gamma_i^{res} \tag{1.26}$$

The activity coefficient contribution of the combinatorial term is given by the following equation:

$$\ln \gamma_i^{com} = \ln\left(\frac{\omega_i}{x_i}\right) + 1 - \frac{\omega_i}{x_i} \tag{1.27}$$

Where x_i is the mole fraction of the component i and ω_i is the modified volume fraction of the component i given by the following equation:

$$\omega_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \tag{1.28}$$

where $r_i = \sum_k \nu_{ki} R_k$ (1.29)

The activity coefficient contribution of the residual term is given by the equation:

$$\ln \gamma_i^{res} = \sum_k \nu_{ki} (\ln \Gamma_k - \ln \Gamma_k^i) \tag{1.30}$$

Where ν_{ki} is the number of groups of type k in molecule i, Γ_k is the activity coefficient of group k at mixture composition and Γ_k^i is the activity coefficient of group k at a group composition corresponding to pure component i. Γ_k and Γ_k^i are given by:

$$\ln \Gamma_k = \frac{z}{2} Q_k \left(-\left[\ln(\sum_m \theta_m \tau_{mk}) \right] + 1 - \sum_i \frac{\theta_i \tau_{ki}}{\sum_j \theta_j \tau_{ji}} \right) \tag{1.31}$$

θ_i is the surface area fraction for component i in the mixture and τ_{ji} is the Boltzmann factor. In modified UNIFAC:

$$\theta_k = \frac{n_k \frac{z}{2} Q_k}{\sum_m n_m \frac{z}{2} Q_m} \tag{1.32}$$

$$\tau_{mk} = \exp(-\alpha_{mk} / T) \tag{1.33}$$

The structural parameters ($\frac{z}{2} Q_k$ and R_k) are given by Larsen et al.[30], n_k is the group mole fraction, given by:

$$n_k = \frac{\sum_i \nu_{ki} x_i}{\sum_i \sum_k \nu_{ki} x_i} \tag{1.34}$$

while the temperature dependent group – interaction parameters α_{mk} are given by:

$$\alpha_{mk} = \alpha_{mk,1} + \alpha_{mk,2}(T - T_0) + \alpha_{mk,3}(T \ln\frac{T}{T_0} + T - T_0) \tag{1.35}$$

T_0 is an arbitrary temperature, here 298.15K while the three coefficients in equation (1.35) are also given by Larsen[30].

1.5. The GERG-water EoS

The GERG-water EoS[31] is an ISO-standard model developed by GERG (Group Europėen de Recherche Gazière) to accurately calculate water content and water dew point for natural gas mixtures. It is the Peng – Robinson equation of state, which in terms of pressure is given by the following equation:

$$P = \frac{RT}{V_m - b} - \frac{\alpha(T)}{V_m^2 + 2bV_m - b^2} \tag{1.36}$$

The energy parameter is given by the following equation:

$$\begin{gathered} \alpha(T) = 0.45724\frac{R^2T_c^2}{P_c}\left[f(T_r)\right]^2 \\ f(T_r) = 1 + \kappa\left(1 - \sqrt{T_r}\right) \\ \kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \end{gathered} \tag{1.37}$$

The co-volume parameter is calculated from:

$$b = 0.0778\frac{RT_C}{P_C} \tag{1.38}$$

When extended the model to mixtures, the classical one fluid mixing rules are used for the energy and co-volume parameters, which are given by equations (1.9) – (1.12). In order, however, to ensure an accurate calculation of water vapor pressure above ice and liquid, the following energy term is used for water:

$$\sqrt{\alpha(T_r)} = 1 + A_1(1 - \sqrt{T_r}) + A_2(1 - \sqrt{T_r})^2 + A_3(1 - \sqrt{T_r})^4 \tag{1.39}$$

The energy term of equation (1.39) is divided in two parts. In the temperature range of 223.15 – 273.16K the energy term is fitted to vapor pressure data above ice (with parameters A_1=0.106025, A_2=2.683845 and A_3=-4.75638), while in the temperature range of 273.16 – 313.15K vapor pressure data over liquid water were used (with parameters A_1=0.905436, A_2=-0.213781 and A_3=0.26005). Finally, in several cases such as water – methane or water – ethane systems a temperature dependent binary interaction parameter is used, which is of the form:

$$k_{ij}(T) = k_{ij,o} + k_{ij,1}\left(\frac{T}{273.15} - 1\right) \tag{1.40}$$

The model can be used for calculations within the temperature range 223.15 – 313.15K. All required coefficients for the calculation of the binary interaction parameter from equation (1.40) as well as the critical component properties that should be used are given by GERG[31] and presented in Appendix C of the thesis.

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Chapter 2.

Application of the Cubic – Plus – Association (CPA) Equation of State to Cross-Associating Systems

2.1. Introduction

Mixtures of associating components, and in particular mixtures of water and alcohols or glycols with hydrocarbons, are of great interest to the oil and gas industry. Methanol is for example commonly used as a hydrate inhibitor during transportation and further processing of natural gas. The accurate description of such systems is a challenging problem of high technological importance for several petrochemical processes. Binary mixtures of lower alcohols are completely miscible with water; as the number of carbons along the chain increases, a characteristic azeotrope occurs.

The CPA EoS has been previously applied to VLE of alcohol – water systems[1,2] over a limited temperature and pressure range (low to moderate pressures), using a binary interaction parameter k_{12} per isotherm. No explicit study of the representation of the azeotropic behavior was conducted. Furthermore the extrapolative capabilities of the model using a single binary interaction parameter (k_{12}) for performing phase equilibrium calculations over an extended temperature and pressure range has not been studied. The extrapolative capabilities are however essential for the design of high pressure distillation processes where, in general, experimental information is scarce.

In this chapter the capability of the CPA EoS to describe VLE of alcohol – water mixtures over an extended temperature and pressure range using a common (temperature independent) interaction parameter is studied. Moreover, for cross – associating systems, different combining rules accounting for the estimation of the cross – association strength have been proposed, as already discussed in chapter 1. The performance of the combining rules is tested to the VLE of lower alcohol – water systems, as well as to higher alcohol – water systems, where increasing immiscibility occurs.

CPA is also extended to SLE of methanol/MEG – water cross – associating systems, assuming complete immiscibility in the solid phase and real solution behavior in the liquid phase. The reason for studying the SLE of those systems is because during the transportation of natural gas, occasionally problems have occurred in concentration areas where, according to the literature, problem – free operation would be expected. Experiments have been carried out which indicate that MEG or methanol at increased pressures and in the presence of hydrocarbons may freeze at higher temperatures than expected, or a solid – complex phase of inhibitor – water might occur. The performance of the different combining rules is further tested for such phase equilibrium calculations; in parallel, the correct in-built temperature dependence of the parameters is also tested to very low temperatures. The freezing curves of the cross – associating systems studied in this work do not form a single eutectic point. Experimental measurements of solid – liquid phase diagrams of selected aqueous glycol or alcohol solutions indicate that at atmospheric pressure and intermediate compositions a solid complex phase is formed[3-7]. A part of this study focuses on the modeling of the complex solid phase as a chemical reaction between alcohol (or glycol) and water.

The association schemes for the components involved in this study are in agreement with previous studies. More specifically, the 2B association scheme is used for alcohols and the 4C association scheme is used for glycols and water.

2.2. Vapor – Liquid Equilibria of alcohol – water systems over extended temperature and pressure ranges

The lower alcohols, except methanol, when mixed with water form an azeotrope. An accurate description of these systems requires both a satisfactory correlation of the phase envelope at various conditions as well as a reasonable calculation of the azeotropic composition. In particular the comparison of the azeotropic composition calculated by the CPA EoS using the different combining rules with the experimental values may lead to useful conclusions. The purpose of this study is two-fold; first to compare the different combining rules in VLE correlations of alcohol – water systems and then to study the possibility of accurate calculations with the use of a common (temperature independent) interaction parameter per system, over an extended temperature and pressure range. The CPA parameters are already presented in chapter 1 (see table 1.4). Table 2.1 presents VLE correlation results for the systems methanol – water, ethanol – water, propanol and isopropanol – water with CPA using CR-1 and ECR combining rule over an extended temperature and pressure range. Similar VLE results for water – n-alcohol systems are presented in table 2.2, using the CR-2, CR-3 and CR-4 combining rules.

The following comments summarize our observations:

1. The CR-2 and CR-4 combining rules systematically fail to correlate the VLE of water – alcohol systems. This observation is in agreement with preliminary results presented in

previous studies[1,2] even though no systematic study of the performance of the combining rules over an extended temperature and pressure range was previously presented. The CR-3 combining rule provides results similar to CR-1; however, the binary interaction parameter is systematically higher than CR-1, as demonstrated in table 2.2. In fact the different combining rules dominate the calculated cross-association strength (given by equation 1.3 in chapter 1) and consequently the overall contribution of the association term within the CPA framework. CR-2, CR-3 and CR-4 not only provide inferior results, compared to CR-1 or ECR, but also lack theoretical justification. As it seems, they provide inadequate mathematical expressions for the calculated cross – association energy and volume. For these reasons, we will further focus on CR-1 and ECR combining rules.

2. The correlation of the methanol – water system is satisfactory with both CR-1 and ECR combining rules, with CR-1 yielding lower values of the interaction parameter. On the other hand, with ECR, a common interaction parameter k_{12} =-0.09 is adequate at all temperatures yielding satisfactory results with errors less than 5% in vapor pressure for the worst case. Typical VLE results for water – methanol system with ECR and a common temperature – independent interaction parameter (k_{12}=-0.09) are presented in figure 2.1.
3. Ethanol – water is an azeotropic system and the combining rules can be further tested by comparing the calculated azeotropic compositions to the experimental ones. Such a comparison, which is presented in table 2.3, shows that ECR provides a more accurate description (than CR-1) of the azeotropic behavior of the system at various conditions. As in the case of methanol – water, very satisfactory results can be achieved with a common interaction parameter k_{12}=-0.11 over the entire temperature and pressure range studied, both in terms of correlation and representation of the azeotropic behavior. The good performance is graphically shown in figure 2.2.
4. Propanol and isopropanol are on the limit of miscibility with water (1-butanol is partially immiscible with water). CR-1 is inferior to ECR for both systems, especially at lower temperatures where the non – ideality is more pronounced; thus ECR provides an adequate description of the azeotropic behavior of isopropanol – water system, as demonstrated in table 2.3. Satisfactory results can be achieved with the use of a common temperature – independent interaction parameter k_{12} = -0.08 for propanol – water system and k_{12} = -0.16 for isopropanol – water system, respectively.

5. The predictive performance of the model (i.e. using k_{12} =0) is usually not adequate, especially at low temperatures where solvation as well as self-association are more pronounced; for instance the error in vapor pressure is about 22% at 298.15K for methanol – water system when CR-1 rule is used (this combining rule yields the smallest error in vapor pressure). Furthermore, CPA EoS often predicts an incorrect phase split for alcohols higher than methanol, making the use of a binary interaction parameter k_{12} (with a value higher compared to alcohol – hydrocarbons) necessary for a qualitatively correct phase behavior.

6. For higher alcohols a characteristic immiscibility region occurs when they are mixed with water. As a result experimental effort is put on LLE rather than VLE measurements. To the best of our knowledge only the VLE of n-butanol – water system is studied at several temperatures, while for other alcohols isobaric VLE measurements at atmospheric pressure are mostly available. VLE correlation results for n-butanol – water using CR-1 and ECR combining rule are presented in table 2.4. CR-1 fails to satisfactorily correlate the system, even when using a binary interaction parameter fitted per isotherm. On the other hand ECR with a temperature independent k_{12} provides adequate VLE calculations, similar to those obtained when the binary interaction parameter (k_{12}) is fitted per isotherm.

The overall conclusion is that the CPA EoS can correlate satisfactorily VLE of low alcohol – water systems over an extended temperature and pressure range with both CR-1 and ECR combining rules. An exception is the VLE of n-butanol – water where CR-1 fails. ECR performs best with a single temperature independent parameter per system providing also a satisfactory description of the azeotropic composition.

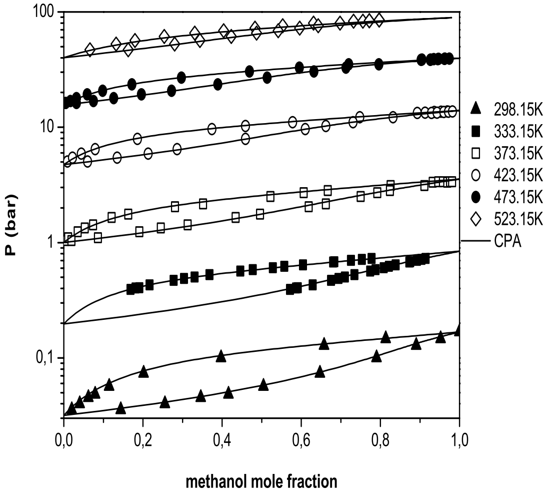

Figure 2.1. VLE for methanol – water with CPA and ECR using k_{12} = -0.09 at all temperatures. Experimental data are taken from the references presented in table 2.1

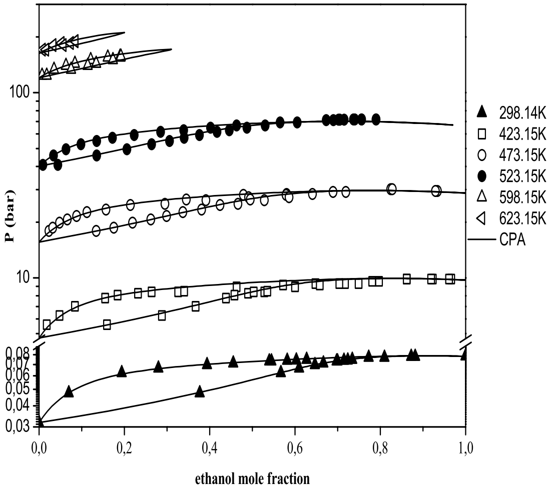

Figure 2.2. VLE for ethanol – water with CPA and ECR using k_{12} = -0.11 at all temperatures. Experimental data are taken from the references presented in table 2.1

Table 2.1. VLE correlation results for water – alcohols over extended temperature and pressure ranges using CR-1 and ECR rules.

System	**Ref**	**T (K)**	**CR-1**			**ECR**			**ECR single k_{12}**		
			k_{12}	**ΔP %**	**Δy * 100**	**k_{12}**	**ΔP %**	**Δy * 100**	**k_{12}**	**ΔP %**	**Δy * 100**
water – methanol	8	298.15	-0.094	1.8	0.6	-0.114	1.1	0.7	-0.09	4.8	1.7
	9	333.15	-0.055	0.6	0.8	-0.088	0.7	0.3	-0.09	0.8	0.4
	10	373.15	-0.051	2.3	0.6	-0.080	3.3	0.8	-0.09	3.5	0.9
	10	423.15	-0.021	0.9	0.8	-0.055	1.6	1.1	-0.09	1.9	1.5
	10	473.15	-0.018	0.8	0.4	-0.054	1.1	0.5	-0.09	2.1	0.8
	10	523.15	-0.017	1.2	1.2	-0.059	0.7	0.9	-0.09	2.4	1.2
water – ethanol	11	298.14	-0.051	3.2	2.1	-0.100	0.9	0.5	-0.11	1.0	0.9
	9	333.15	-0.036	1.4	1.6	-0.096	1.9	0.5	-0.11	1.9	1.2
	12	343.15	-0.041	1.6	1.2	-0.089	2.1	0.7	-0.11	2.6	1.5
	12	363.15	-0.036	1.3	1.0	-0.087	2.2	0.8	-0.11	2.6	1.5
	13	423.15	-0.038	1.2	1.1	-0.105	2.6	1.2	-0.11	2.6	1.3
	13	473.15	-0.042	1.3	0.9	-0.105	2.1	0.9	-0.11	2.1	0.9
	13	523.15	-0.042	2.8	0.8	-0.112	1.7	0.6	-0.11	1.7	0.6
	13	598.15	-0.087	1.5	1.9	-0.132	0.9	1.7	-0.11	0.9	2.1
	13	623.15	-0.103	2.4	1.5	-0.137	1.8	1.7	-0.11	1.7	2.0
water – propanol	8	298.15	-0.038	6.3	3.9	-0.083	1.9	1.2	-0.08	1.9	1.3
	14	333.15	-0.007	3.7	3.3	-0.079	0.8	0.6	-0.08	0.7	0.7
	15	363.15	-0.013	3.5	2.8	-0.085	1.2	1.0	-0.08	1.8	1.2
water – isopropanol	16	298.15	-0.092	5.5	3.2	-0.152	1.5	0.6	-0.16	1.4	1.2
	17	353.15	-0.066	3.6	2.8	-0.128	1.6	0.6	-0.16	4.8	2.6
	13	423.15	-0.051	1.8	2.2	-0.128	3.8	1.4	-0.16	3.2	2.2
	13	473.15	-0.062	1.8	1.4	-0.146	2.4	0.6	-0.16	2.3	0.8
	13	523.15	-0.081	1.3	1.5	-0.166	1.4	0.7	-0.16	1.8	0.6
	13	548.15	-0.082	0.7	1.6	-0.17	1.6	0.5	-0.16	2.0	0.5
Average error				**2.2**	**1.6**		**1.7**	**0.8**		**2.2**	**1.2**

Table 2.2. VLE correlation results for water – alcohols over extended temperature and pressure ranges using CR-2 and CR-3 and CR-4 rules.

System	**Ref**	**T (K)**	**CR-2**			**CR-3**			**CR-4**		
			k_{12}	**ΔP %**	**Δy * 100**	**k_{12}**	**ΔP %**	**Δy * 100**	**k_{12}**	**ΔP %**	**Δy * 100**
water – methanol	8	298.15	-0.024	5.9	1.9	-0.138	1.6	1.1	-0.068	3.3	1.0
	9	333.15	0.065	5.2	2.9	-0.119	1.9	0.7	-0.004	2.5	1.6
	10	373.15	0.049	2.3	1.8	-0.102	4.0	1.1	-0.001	1.1	0.1
	10	423.15	0.093	2.1	1.3	-0.072	2.0	1.3	0.042	1.2	0.6
	10	473.15	0.106	2.4	1.5	-0.066	1.2	0.5	0.056	1.6	1.0
	10	523.15	0.122	3.8	2.6	-0.067	0.6	0.9	0.072	2.8	2.1
water – ethanol	11	298.14	0.073	15.5	9.7	-0.069	1.9	1.3	0.059	13.9	8.7
	9	333.15	0.122	11.7	8.4	-0.055	0.6	1.0	0.105	10.5	7.5
	12	343.15	0.122	11.6	8.5	-0.056	0.9	0.6	0.104	10.5	7.6
	12	363.15	0.092	10.0	6.2	-0.051	0.6	0.5	0.079	9.1	5.6
	13	423.15	0.136	8.7	6.3	-0.055	1.3	0.8	0.121	7.8	5.8
	13	473.15	0.137	7.5	5.1	-0.057	1.2	0.8	0.123	6.9	4.7
	13	523.15	0.187	8.6	3.5	-0.056	2.5	0.7	0.142	8.4	3.2
	13	598.15	0.107	6.8	6.9	-0.085	0.9	2.1	0.094	1.2	1.2
	13	623.15	0.072	2.1	1.3	-0.114	2.5	1.5	0.058	2.2	1.3
water – propanol	8	298.15	0.031	15.3	11.0	-0.046	5.2	3.1	0.024	14.5	10.3
	14	333.15	0.111	12.9	10.9	-0.019	2.9	2.6	0.101	12.1	10.2
	15	363.15	0.102	12.5	11.4	-0.025	2.8	2.2	0.094	11.6	10.6
Average error				**8.8**	**6.2**		**1.8**	**1.2**		**7.6**	**5.3**

Table 2.3. Experimental and calculated azeotropic composition for two alcohol (1) – water (2) systems

system	T (K)	Ref	experimental		CR-1 & k_{12} optimum		ECR & k_{12} optimum		ECR single k_{12}	
			x(1)	P / bar	x(1), calc	P calc / bar	x(1), calc	P calc / bar	x(1), calc	P calc / bar
ethanol – water	333.15	9	0.91	0.4705	0.997	0.4758	0.892	0.4805	0.92	0.4780
	343.15	12	0.9092	*NA*	0.997	0.7346	0.874	0.7442	0.917	0.7384
	363.15	12	0.8845	*NA*	0.995	1.6035	0.89	1.6291	0.90	1.6144
	523.15	13	0.756	71.7055	0.73	67.7571	0.72	69.5963	0.72	69.6788
isopropanol - water	353.15	17	0.6764	1.0041	0.6875	0.9346	0.6725	1.0173	0.71	0.9893
	423.15	13	0.6775	9.1014	0.635	8.8818	0.65	9.5056	0.68	9.2930
	473.15	13	0.6435	27.9246	0.61	27.0778	0.63	28.7202	0.64	28.4811

NA: not available

Table 2.4. VLE correlation results for n-butanol – water over extended temperature and pressure ranges using CR-1 and ECR rules.

System	Ref	T (K)	CR-1			ECR			ECR single k_{12}		
			k_{12}	ΔP %	Δy * 100	k_{12}	ΔP %	Δy * 100	k_{12}	ΔP %	Δy * 100
water – n-butanol	8	298.15	-0.044	9.0	3.6	-0.108	3.0	1.5	-0.096	3.8	0.7
	18	363.15	-0.018	7.8	3.6	-0.081	3.0	1.8	-0.096	3.7	2.9
	18	383.15	-0.014	8.0	3.6	-0.078	1.5	1.5	-0.096	2.7	2.6
	18	403.15	-0.015	7.2	3.8	-0.085	1.5	1.1	-0.096	1.9	1.6
Average error				**8.0**	**3.7**		**2.3**	**1.5**		**3.0**	**2.0**

2.3. Liquid – Liquid equilibria of heavy alcohol – water systems

Heavy alcohols (butanol and higher) are immiscible with water. The performance of CPA has been tested for 1-butanol – water, 1-pentanol – water, the environmentally important 1-octanol – water system and 1-dodecanol-water. The CPA pure component parameters are presented in chapter 1. The binary interaction parameter k_{12} is, for each system, determined from the experimental solubility of the alcohol in the aqueous phase. Table 2.5 shows the percentage average absolute deviation (% AAD) of water solubility in the alcohol phase with CR-1 and ECR. ECR is, in these cases, systematically inferior to CR-1. This is further elucidated by figure 2.3, which presents the LLE correlation for 1-octanol – water with the two combining rules. ECR underestimates the solubility of water in 1-octanol. On the other hand, CR-1 provides adequate correlation of both solubilities, with a single value of the interaction parameter. Similar behavior is obtained for the other systems. The other combining rules (CR-2, CR-3 and CR-4) are also tested but all of them fail to correlate both solubilities with the same binary interaction parameter (k_{12}). Thus CR-1 was found to be the only choice for water – alcohol LLE.

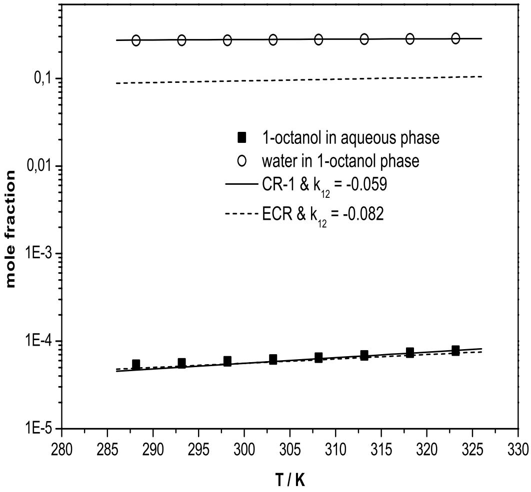

Figure 2.3. LLE correlation results for 1-octanol – water with CPA and different combining rules. Experimental data are taken from Dallos et al.[20].

Table 2.5. Alcohol – water liquid – liquid equilibria using an interaction parameter k_{12} obtained from the experimental solubility of the alcohol in the aqueous phase

System	Ref	CR-1		ECR	
		k_{12}	**%AAD x_W**	**k_{12}**	**%AAD x_W**
1-butanol – water	19	-0.065	5.6	-0.081	33.5
1-pentanol – water	19,21	-0.037	13.7	-0.054	40.1
1-octanol – water	20	-0.059	0.9	-0.082	65.4
1-dodecanol – water	21	-0.113	27.7	-0.136	63.9

2.4. Solid – Liquid Equilibria of methanol and MEG – water systems, including the solid complex phase

In this section CPA is extended to SLE of the binary systems MEG – water and methanol – water. Both systems form a stable solid – complex phase at intermediate concentrations, but initially the focus is only on modeling the freezing curves of the pure components. The working equation of the SLE at low pressures is, assuming complete immiscibility in the solid phase and real solution behavior in the liquid phase[22]:

$$x_i \gamma_i = \exp\left[\frac{\Delta H_i^{fus}}{RT_{mi}} \left(1 - \frac{T_{mi}}{T}\right) + \frac{\Delta Cp_i}{R}\left(\frac{T_{mi}}{T} - 1 - \ln\frac{T_{mi}}{T}\right)\right] \qquad (2.1)$$

Table 2.6 presents the values of the melting temperature $T_{m,i}$, the heat of fusion (ΔH_i^{fus}) at $T_{m,i}$ and the difference in heat capacity ΔCp_i for the compounds involved in this study. The effect of ΔCp_i is small and usually not taken into consideration in equation (2.1), since in most cases it does not affect the calculations. This is found to be the case for MEG and methanol, probably due to the limiting temperature range, but the use of ΔCp_i for water improves the results. Figure 2.4 presents calculations assuming that the solid phase is pure and the liquid phase is ideal (i.e. $\gamma_i = 1$), showing the effect of using ΔCp_i for water. Furthermore, the ideal behavior assumption is found to provide reasonable results for such a complex system (excluding the intermediate solid complex phase) in both phases, because the experimental activity coefficients are relatively close to unity (about 0.8 for water and unity for MEG freezing curve). Similar is the performance for methanol – water, where once again the assumption of the ideal behavior performs adequate.

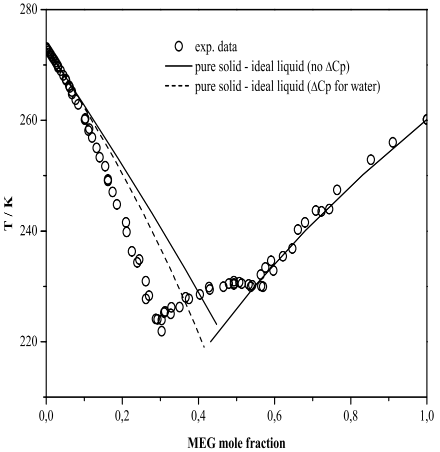

Figure 2.4. SLE calculations for MEG – water assuming pure solid and ideal liquid behavior.

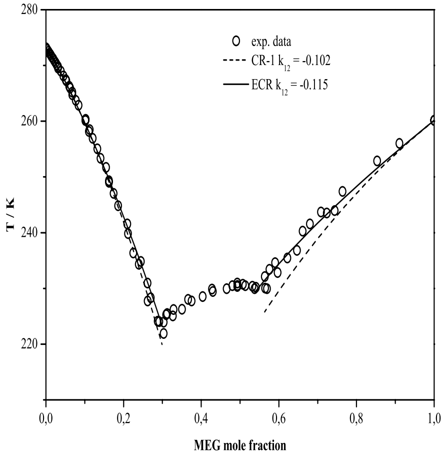

Figure 2.5. SLE correlation results for MEG – water with CPA using CR-1 or ECR rule.

For the MEG – water system, it is found that only ECR successfully correlates both freezing curves, using a single, temperature independent binary parameter, while all other combining rules fail. Figure 2.5 presents correlation results for MEG – water system using both CR-1 and ECR combining rules and fitting the binary interaction parameter to the water freezing curve. Furthermore, the SLE calculations with ECR can be considered extrapolation, since the k_{12} used (-0.115) is obtained from VLE correlation at 343.15 and 363.15K[2]. The predictive performance of the model (k_{12}=0) is however not satisfactory, demonstrating a behavior similar to the one presented for the VLE prediction of the system by Derawi et al[2]. Typical SLE prediction and correlation results for MEG – water with ECR are demonstrated in figure 2.6. The performance of SRK-MC is also tested. It is found that even though MC-SRK requires a smaller value of binary interaction parameter (k_{12}) for correlating the water freezing curve, as is the case for the VLE of the system[2], the freezing curve of MEG is not correlated as adequate as with CPA and ECR.

The SLE prediction for methanol – water is similar to that for MEG – water and the use of a binary interaction parameter is required for satisfactory calculations of the freezing curves. However, in this case, both ECR and CR-1 combining rules correlate satisfactorily both freezing curves, using slightly different values of binary interaction parameters (k_{12}=-0.147 with CR-1 and

k_{12}=-0.153 with ECR). The MC-SRK EoS can also satisfactorily correlate both freezing curves in the case of this binary system using a binary interaction parameter k_{12}=-0.121. Unlike MEG – water, in this case a different binary interaction parameter should be used for an adequate correlation of the SLE of the system with ECR. The use of ECR and k_{12}=-0.09 does not even enable satisfactory calculations of the freezing curve of water for temperatures lower than 260K.

The use of other combining rules (CR-2, CR-3, CR-4) is of no practical importance, since none of them can correlate both freezing curves for MEG – water binary system, while for the case of water – methanol all three of them perform very similar to CR-1 or ECR when fitting the k_{12} to water freezing curve.

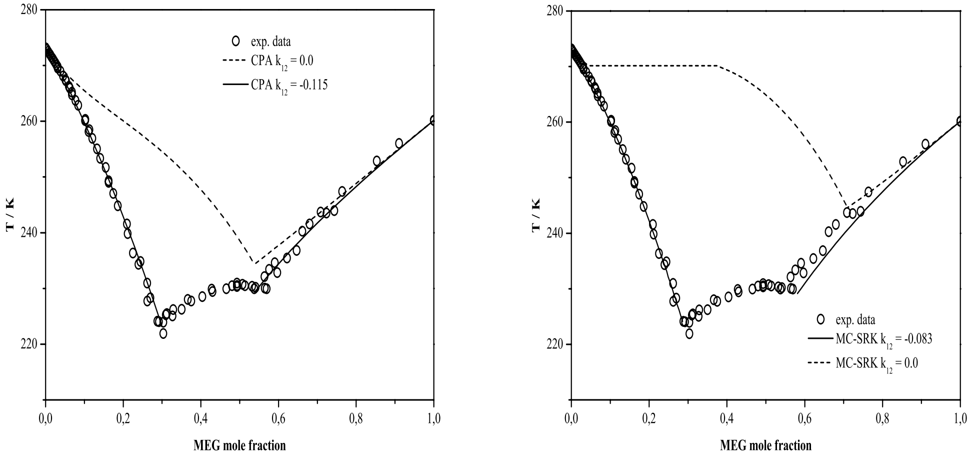

Figure 2.6. SLE prediction and correlation results for MEG – water with CPA and ECR. Experimental data are taken from Cordray[3] and Ott[4]. On the right site SLE calculations with MC-SRK are also presented.

Table 2.6. Values of $T_{m,i}$, ΔH_i^{fus} at $T_{m,i}$ and ΔCp_i for the compounds involved in this study.

Compound	$T_{m,i}$ (K)	ΔH_i^{fus} (J . mol^{-1})	ΔCp_i (J/mol*K)	Reference
water	273.15	6010	37.29	23
MEG	260.15	9958	-	24,3
methanol	175.25	3177	-	25
1-butanol	183.35	9282	-	26

At atmospheric pressure and in a narrow composition range an aqueous solution of MEG or methanol forms a solid complex, when it freezes out. The complex is assumed to have a crystal lattice structure and the formation of the solid complex can thus be modeled as the product of the interaction between MEG/methanol and water. We consider in general the following interaction between two liquids A and B forming a solid A.B:

$$A \cdot B_{(s)} \leftrightarrow A_{(l)} + B_{(l)}$$

Assuming that the solid complex behaves as a pure solid, the activity of the complex will be unity. The chemical equilibrium constant (*K*) for the interaction can be calculated as:

$$K = \gamma_A \cdot x_A \cdot \gamma_B \cdot x_B \tag{2.2}$$

The temperature dependency of the chemical equilibrium constant, at constant pressure, can be derived from the Gibbs-Helmholtz equation.

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right] = -\frac{\Delta H}{T^2} \tag{2.3}$$

And given that

$$\Delta G = -RT \ln K \tag{2.4}$$

The equation of the temperature dependence of *K* at constant pressure is:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{2.5}$$

Assuming that ΔH is a function of temperature, it can be described in the following manner:

$$\Delta H(T) = \Delta H^{ref} + \int_{T^{ref}}^{T} \Delta C_p dT \tag{2.6}$$

Where ΔC_p is the difference in heat capacity and ΔH^{ref} is the enthalpy of fusion of the solid complex phase at a given reference temperature T^{ref}. Furthermore if it is assumed that ΔC_p is zero in the relatively small temperature area where the solid complex is formed, the following expression is obtained:

$$R \ln K = R \ln K^{ref} + \Delta H^{ref}\left(\frac{1}{T^{ref}} - \frac{1}{T}\right) \tag{2.7}$$

The mixture properties in the liquid phase are obtained from CPA using ECR and the interaction parameters regressed from experimental data of the freezing curves of the pure MEG/methanol and water. ECR is preferred as it describes equally well SLE and VLE of both systems. The interaction parameters are k_{12}= -0.115 for the MEG – water system and k_{12}= -0.153 for the methanol – water system, respectively, in accordance to the results presented previously.

Modeling of the solid complex in this manner requires that the molar composition of the complex is known. The freezing diagram of the MEG – water system has been extensively studied in the literature with particular emphasis to the intermediate concentrations, where the solid complex occurs; the formation of a 1:1 molar composition complex is concluded[3,4]. The formation of a similar 1:1 solid complex is also reported for the methanol – water system[5,7]. Finally, the enthalpy of fusion of the complex phase ΔH^{ref} is regressed from experimental data of the solid complex phase, whereas the value of the equilibrium constant K^{ref} at a chosen reference temperature T^{ref} is calculated from equation (2.2). Table 2.7 presents the values of the equilibrium constant K^{ref} at a chosen reference temperature T^{ref} and the optimized value for the enthalpy of fusion of the complex phase ΔH^{ref} for each system studied.

Literature values for such complex solid phases are very rare. A typical system forming such a solid complex phase is the system acetone – chloroform, which is also suggested to form a solid complex with 1:1 stoichiometric ratio[22]. Prausnitz[22] estimates the enthalpy of fusion for the solid complex of acetone – chloroform to be 11370 J/mol which is in fair agreement to the values suggested in table 2.7 for MEG – water and methanol – water respectively.

Figures 2.7 and 2.8 present the complete freezing diagram of the MEG – water and methanol – water systems, respectively. The calculated eutectics for the MEG – water system are at 223.95 K and 229.49 K and mole fractions of 0.30 and 0.54 of ethylene glycol, respectively. These results are in good agreement with the experimental values[4] which are reported to be 224.12 K and 230.22 K and mole fractions 0.288 and 0.541 of ethylene glycol, respectively. Similar results are obtained for methanol. The calculated eutectics are at 171.25 K and 159.23 K and mole fractions of 0.55 and 0.79 of methanol, respectively, while an experimental eutectic is reported[7] to be at 157 K and 0.807 of mole fraction of methanol.

Table 2.7. Values of the parameters used in equation (2.7)

System	T^{ref} **[K]**	K^{ref}	ΔH^{ref} **[J mol^{-1}]**
MEG – water	223.95	0.168048	14450
Methanol - water	171.25	0.208059	8540

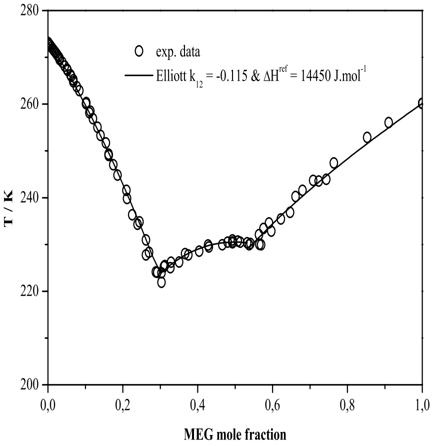

Figure 2.7. SLE correlation of MEG – water using CPA and ECR with a common interaction parameter k_{12} = -0.115.

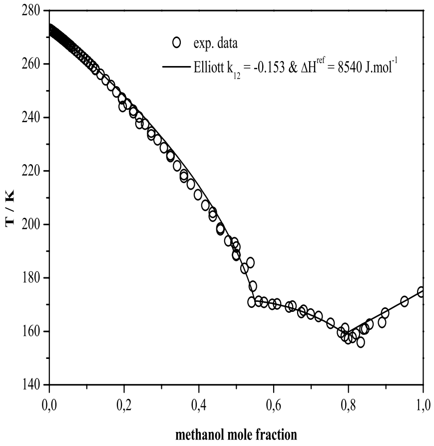

Figure 2.8. SLE correlation of methanol – water using CPA and ECR with a common interaction parameter k_{12} = -0.153.

2.5. VLE of alcohol – water systems with SRK/MHV2 using modified UNIFAC

Comparisons to other thermodynamic models are always useful for the evaluation of the performance of a model, especially when compared to more conventional engineering models for handling polar mixtures. In this section the performance of CPA is compared to SRK using MHV2 mixing rule and the modified UNIFAC of Larsen to calculate the excess Gibbs energy (G^E) in the expression of the MHV2 mixing rule. The reason for choosing this model is because this was shown to perform quite satisfactorily for high pressure VLE of water – alcohol systems[27]. Finally all modified UNIFAC parameters are as reported from Larsen et al.[28]. A complete presentation of the model can be found is section 1.4. Finally, a Mathias – Copeman expression is used for the pure component energy parameter (α_i) as discussed in chapter 1. All parameters for the Mathias – Copeman expression are taken by Dahl et al.[29] and tabulated in table 2.8 for the components involved in this study.

VLE results for alcohol – water binary systems using SRK/MHV2 with the modified UNIFAC are presented in table 2.9. For comparison the results of CPA using ECR and a common temperature independent binary interaction parameter (all values taken from table 2.1) are also shown. CPA using only one binary interaction parameter provides better results for methanol – water at high temperatures and propanol – water at low temperatures, while the results are overall equally satisfactory for ethanol – water and isopropanol – water. For the same calculations three parameters are required for SRK/MHV2 with modified UNIFAC which are the three coefficients in equation (1.34) in section 1.4. Typical results are presented in figures 2.9 and 2.10.

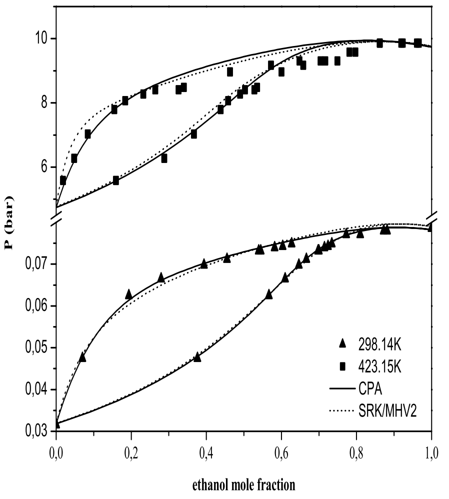

Figure 2.9. VLE for ethanol – water with SRK/MHV2 using modified UNIFAC and CPA with ECR using k_{12} = -0.11 at both temperatures.

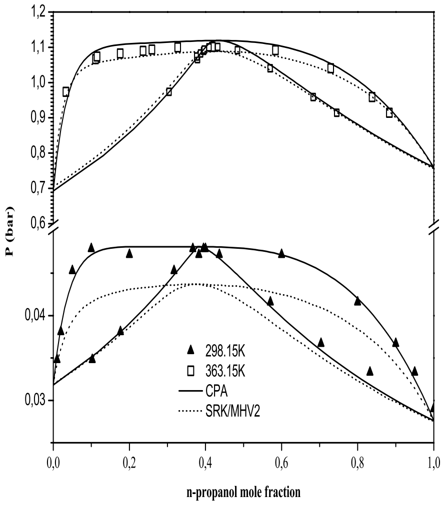

Figure 2.10. VLE for n-propanol – water with SRK/MHV2 using modified UNIFAC and CPA with ECR using k_{12} = -0.08 at both temperatures.

Table 2.8. Pure component parameters for the Mathias – Copeman expression of the energy parameter (eq. 1.20).

Compound	Q_1	Q_2	Q_3
water	1.0873	-0.6377	0.6345
methanol	1.4550	-0.8150	0.2486
ethanol	1.4252	0.1898	-1.3014
n-propanol	1.2645	1.2138	-2.4077
i-propanol	1.3542	0.9546	-2.1524

Table 2.9. VLE correlation results of water – alcohols with SRK/MHV2 using modified UNIFAC and the CPA EoS.

			SRK/MHV2		CPA EoS		
System	**Ref**	**T (K)**	**ΔP %**	**Δy * 100**	**k_{12}**	**ΔP %**	**Δy * 100**
water – methanol	8	298.15	1.8	0.6	-0.09	4.8	1.7
	9	333.15	0.5	0.3	-0.09	0.8	0.4
	10	373.15	4.2	1.7	-0.09	3.5	0.9
	10	423.15	3.0	2.0	-0.09	1.9	1.5
	10	473.15	7.1	3.2	-0.09	2.1	0.8
	10	523.15	16.2	3.8	-0.09	2.4	1.2
water – ethanol	11	298.14	1.3	1.0	-0.11	1.0	0.9
	9	333.15	1.5	0.6	-0.11	1.9	1.2
	12	343.15	1.5	0.8	-0.11	2.6	1.5
	12	363.15	1.6	0.8	-0.11	2.6	1.5
	13	423.15	3.3	0.8	-0.11	2.6	1.3
	13	473.15	2.8	2.2	-0.11	2.1	0.9
	13	523.15	3.9	2.6	-0.11	1.7	0.6
	13	598.15	1.4	0.9	-0.11	0.9	2.1
	13	623.15	0.5	0.1	-0.11	1.7	2.0
water – propanol	8	298.15	8.5	3.8	-0.08	1.9	1.3
	14	333.15	5.0	2.5	-0.08	0.7	0.7
	15	363.15	1.8	1.4	-0.08	1.8	1.2
water – i-propanol	16	298.15	1.2	1.6	-0.16	1.4	1.2
	17	353.15	2.0	1.2	-0.16	4.8	2.6
	13	423.15	5.3	2.0	-0.16	3.2	2.2
	13	473.15	5.4	2.9	-0.16	2.3	0.8
	13	523.15	6.9	4.5	-0.16	1.8	0.6
	13	548.15	7.8	3.5	-0.16	2.0	0.5
Average			**3.7**	**1.8**		**2.2**	**1.2**

2.6. Discussion – Comparison to previous studies

The application of CPA to phase equilibria of cross – associating alcohol/glycol – water systems presented in this work and previous studies[1,2] shows that the performance of the model depends both on the combining rule chosen for the cross – association strength (ECR, CR-1 etc.) and on the type of phase equilibria (VLE, LLE, SLE). Some combining rules perform satisfactorily for some types of phase equilibria but fail in others. For instance, ECR with a common temperature independent interaction parameter provides very adequate VLE correlations of alcohol – water systems and SLE correlation of the methanol – water system, over an extended temperature and pressure range, but fails to correlate the LLE of alcohol – water systems.

Table 2.10 summarizes the results, i.e. which combining rule performs best for various systems and types of phase equilibria. If both CR-1 and ECR perform satisfactorily, then they are both mentioned. In particular we observe that:

1. ECR is the best choice for VLE of lower alcohol – water binary systems; CR-1 provides an alternative, yielding however an inferior representation of the azeotropic behavior. ECR is also the best combining rule for the SLE of methanol – water.

2. Regarding LLE of alcohol – water systems, CR-1 is the only successful combining rule for representing both solubilities using the same interaction parameter. Prediction of VLE using the combining rule and the binary interaction parameter (k_{12}) obtained from LLE is a very robust test of the performance of the model. Typical VLE predictions using CR-1 for 1-butanol – water (k_{12}= -0.065) are shown in figure 2.11, while figure 2.12 presents VLE calculations for pentanol – water using CR-1 and k_{12}= -0.037 optimized from LLE data. The model can correlate the LLE with a single k_{12} (though not the closed loop area), but the VLE is somewhat poorly predicted. It is already shown in table 2.4 that CPA using ECR and k_{12}=-0.096 can correlate the VLE of n-butanol–water over an extended temperature range. The use of ECR with k_{12}=-0.096 correlates very satisfactory the Txy data at atmospheric pressure, demonstrating a performance very similar to SRK/MHV2 and modified UNIFAC, which is also presented in figure 2.11. LLE/VLE calculations for the two systems with SRK/MHV2, using UNIFAC parameters optimized from VLE data, are also presented in figures 2.11 and 2.12. Using UNIFAC parameters optimized from VLE data provide very poor LLE results.

3. SLE of heavy alcohol – water systems may sometimes require slightly different (than VLE/LLE) interaction parameters. Lohmann et al.[26] measured the freezing diagram of butanol – water system over an extended range of butanol mole fraction, without reporting any solid – complex formation. The correlation of SLE of this binary system with the CPA EoS using CR-1 and an interaction parameter k_{12} =-0.065 regressed from LLE data is presented in figure 2.13. CR-1 does not provide an adequate correlation of the system. In addition, SLE calculations with CR-1 and ECR and an optimum interaction parameter, respectively, are presented. The values of $T_{m,i}$, ΔH_i^{fus} at $T_{m,i}$ and ΔCp_i used are presented

in table 2.6. The use of CR-1 overestimates the characteristic miscibility gap of the system when k_{12} is fitted to SLE data, while adequate correlation is achieved with ECR and a single interaction parameter. Furthermore the calculations seem to be sensitive to the binary interaction parameter used, since ECR and k_{12}=-0.096 (optimized from VLE data) performs quite different than ECR and k_{12}=-0.096 (optimized from SLE data). Poor is however the LLE correlation of the system using ECR and the optimized k_{12} either from VLE (-0.096) or SLE (-0.115), as figure 2.14 demonstrates.

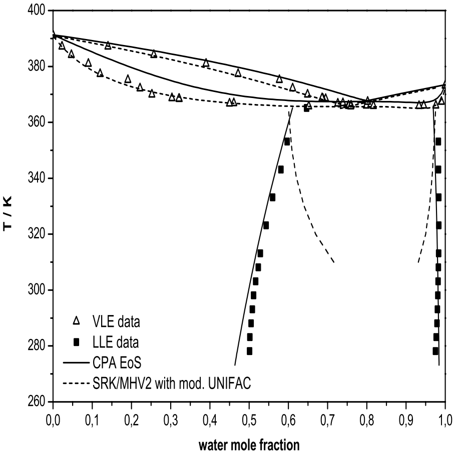

Figure 2.11. VLE and LLE for n-butanol-water using SRK/MHV2 with mod. UNIFAC and CPA with CR-1 and k_{12}=-0.065 optimized from LLE data. Experimental data are from DECHEMA[19] and Hessel et al.[30]

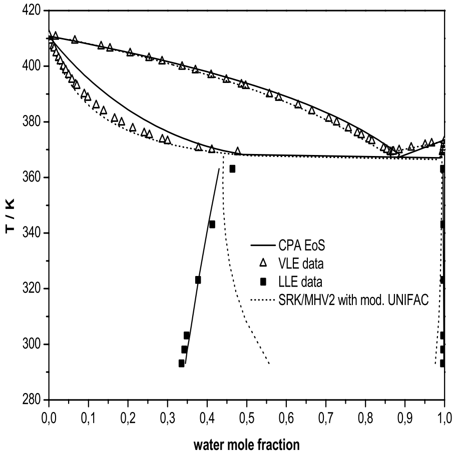

Figure 2.12. VLE and LLE for n-pentanol-water using SRK/MHV2 with mod. UNIFAC and CPA with CR-1 and k_{12}=-0.037 optimized from LLE data. Experimental data are from DECHEMA[19,31].

4. For the glycol – water systems Derawi et al.[2] showed that CR-1 is the best predictive choice for VLE of MEG – water system. CPA with ECR and a single interaction parameter can successfully correlate VLE, providing similar results to the CR-1 rule, requiring however a higher binary interaction parameter. Nevertheless, for SLE, ECR is the only choice for adequate correlations of both freezing curves with a temperature

independent value of the interaction parameter, which is the same value used for VLE calculations. Use of CR-1 fails to correlate both freezing curves.

Table 2.10. Best combining rules per case/system for the CPA EoS.

System	***VLE***	***LLE***	***SLE***
methanol – water	ECR (or CR-1)	-	ECR (or CR-1)
ethanol - water	ECR (or CR-1)	-	-
propanol - water	ECR (or CR-1)	-	-
isopropanol - water	ECR (or CR-1)	-	-
1-butanol – water	-	CR-1	ECR
1-pentanol – water	-	CR-1	-
1-octanol - water	-	CR-1	-
1-dodecanol – water	-	CR-1	-
MEG – water	CR-1 (or ECR)	-	ECR
DEG – water	CR-1	-	-
TEG – water	CR-1	-	-

5. The CPA interaction parameters are close to zero (usually slightly positive) for systems having only self-associating compounds e.g. alcohol – alkanes[32]. On the other hand the parameters are negative and rather large for cross-associating systems e.g. alcohols/glycols – water, irrespectively, in most of the cases, of the combining rule used. This is not only the case just for the SLE type systems, where due to the low temperatures the hydrogen bonding is more pronounced, but also for VLE of alcohol (or glycol) – water. These large negative interaction parameters indicate that the association term of CPA underestimates the degree of cross-association (solvation) of these systems.

6. For aqueous solutions of methanol and MEG, components of major importance to the oil and gas industry, ECR is the most successful rule. The performance of ECR is very satisfactory for both VLE and SLE. Especially for the SLE of MEG – water system the value of the interaction parameter (k_{12} = -0.115) is the one obtained from VLE correlations at 343.15K and 363.15K[2].

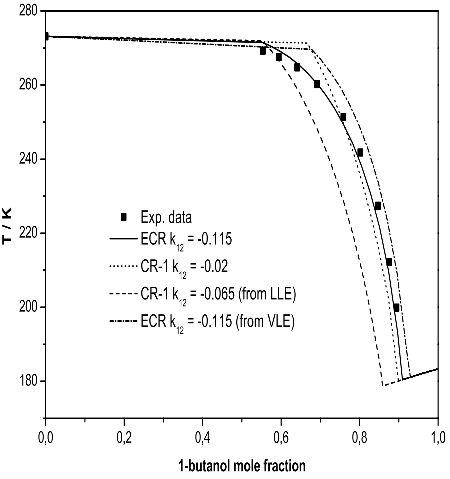

Figure 2.13. SLE correlations for the system n-butanol – water with the CPA EoS and different combining rules. Exp. data from Lohman et al.[26].

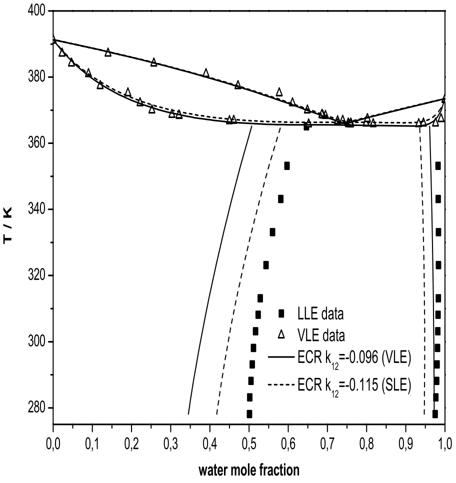

Figure 2.14. VLE and LLE for n-butanol-water using CPA with ECR and k_{12} optimized from SLE or VLE data. Experimental data are from DECHEMA[19] and Hessel et al.[30]

2.7. Conclusions

The performance of the CPA EoS to binary alcohol – water cross – associating systems with the use of different combining rules for estimating the cross – association strength $\Delta^{A_iB_j}$ was studied. For lower alcohols which are completely miscible with water, it was concluded that ECR provides the most adequate description, both with respect to the correlative performance and the representation of the azeotropic behavior. Furthermore, very satisfactory results can be achieved with a common temperature-independent binary interaction parameter over an extended temperature and pressure range, implying that the model can be used safely for inter/extrapolations at different conditions. For higher alcohols which are not miscible with water, CR-1 provides a satisfactory correlation of the mixtures, while ECR fails. The vapor – liquid and solid – liquid equilibria of the industrially important methanol – water and MEG – water systems can be described satisfactorily with CPA using ECR and a single interaction parameter (k_{12}). The solid complex phase which occurs at intermediate concentrations of methanol or MEG can be successfully computed as a chemical reaction, enables calculations of the complete freezing diagram of these systems. The results obtained with the CPA EoS are shown to be similar and occasionally better compared to SRK/MHV2 with modified UNIFAC.

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Chapter 3.

Evaluation of Association Schemes for Water and Alcohols

3.1. Introduction

In Chapter 2 the CPA EoS was applied to VLE and LLE of cross – associating alcohol – water systems. Additionally, some SLE results for MEG – water and methanol – water systems were presented. Although the correlative performance of CPA was successful for these cross – associating systems, three drawbacks remain: a) different combining rules are needed for correlating different types of phase equilibria e.g. the CR-1 is the only choice for water-heavy alcohol LLE and ECR is the only choice for water-MEG SLE, b) the interaction parameters for cross-associating systems e.g. alcohol-water or glycol-water are considerably higher than the much more non-ideal alcohol-alkane and glycol-alkane systems[1,2] c) The values of the interaction parameters are systematically negative, indicating that the cross-association is underestimated. Furthermore, even if good description is obtained when a binary interaction parameter is used, the prediction (k_{12}=0) is often unsatisfactory even with nearly ideal systems e.g. water-methanol.

In an effort to understand and hopefully solve these problems, an investigation of the association schemes for water and alcohols has been made. Within the CPA framework, the 4C association scheme has been previously assigned for water[3,4] and the 2B association scheme for alcohols[1]. Although the choice of the 4C association scheme for water was reported to be due to the superior LLE correlative performance of water – HC systems[3], the 2B scheme for alcohols was adopted without comparison against the more rigorous 3B association scheme. Additionally, the 4C association scheme for water and the 2B for alcohols are somehow "inconsistent", in the sense that for water the 2 lone pairs of oxygen are considered to be two independent sites while in the case of the 2B scheme for alcohols those merge to one site.

For these reasons, a re–examination of the association scheme of water is initially presented in section 3.2 while the rest of the chapter deals with the investigation of the implementation of the rigorous correct 3B scheme for alcohols, a study not previously performed for CPA

3.2. The association scheme of water

Water and in general aqueous systems are extremely important in many applications in oil, gas and chemical industry. Given that it is of great importance to describe the properties of such systems accurately, this section focuses on how many association sites water molecule actually has within the CPA framework. Both schemes tested in this section (3B and 4C) seem to have a reasonable physical justification, and have been extensively used within the SAFT framework.

Many researchers e.g. Sandler, Donohue, Economou, Elliott, Suresh refer to the work of Wei et al.[5] where it is indicated that “in the clusters of liquid water only three sites are bonded per molecules, indicating that water should be treated with the 3B association scheme”. Economou & Donohue[6] state that “although each water molecule is capable of forming up to 4 hydrogen bonds, because of the geometry of the water molecule and structure of the 3D networks which are formed, most water molecules have three of fewer hydrogen bonds”. The 3B association scheme was adopted in many of these investigations as for example by Fu and Sandler[7], SAFT by Huang and Radosz[8] or by Wu & Prausnitz[9] in their PR-CPA EoS (Peng-Robinson is used for accounting for the physical interactions). PC-SAFT water parameters recently presented by Gross and Sadowski[10] are based on the even simpler 2B scheme, but this has only been tested to a few cross-associating systems of water with alcohols and not for water-alkanes.

In their investigations with SAFT, Wolbach and Sandler[11,12] using two different ab-initio molecular orbital methods for estimating SAFT parameters, have concluded that the 4C scheme is actually better than 3B for water. Many recent investigations with SAFT indicate that water should be treated as a four-site molecule[13-15].

CPA was previously shown[3,4,16,17] to describe water-alkanes LLE very satisfactorily (both the water and hydrocarbon solubilities) with a single temperature independent interaction parameter using the 4C association scheme for water. As mentioned previously, the scope of this section is to investigate the possibility of implementing the 3B association scheme for water with CPA, since this scheme can be as well theoretically supported from the aforementioned analysis. Various sets of water pure compound parameters using the 3B association scheme and the well established pure compound parameters for the 4C scheme for water[4] are presented in table 3.1. Although all sets of water parameters presented in table 3.1 fit equally satisfactory vapor pressure and liquid density experimental data of water, only the 4C association scheme can satisfactorily correlate the LLE of water – hydrocarbons, as typically presented in figure 3.1 for water – hexane. This conclusion is in agreement to the previously presented results[3], suggesting that within the CPA framework the 4C association scheme is the only successful choice for the water molecule.

Table 3.1. Different sets of CPA parameters for 3B water for the temperature range Tr = 0.55 – 0.90. The 4C pure compound parameters for water are taken by Kontogeorgis[4]. (T_c=647.29K)

Scheme	a_0 **(bar l^2 mol^{-2})**	b **(l/mol)**	c_1	ε^{AB} **(bar l mol^{-1})**	β^{AB} ***10^3**	**ΔP** **(%)**	**Δρ** **(%)**
3B (set1)	3.006	0.01497	0.3592	207.97	21.3	0.4	0.1
3B (set2)	3.242	0.01537	0.7017	141.55	61.9	0.5	0.5
3B (set3)	2.879	0.01463	0.0787	250.00	10.8	0.6	0.4
4C	1.228	0.01452	0.6736	166.55	69.2	0.8	0.5

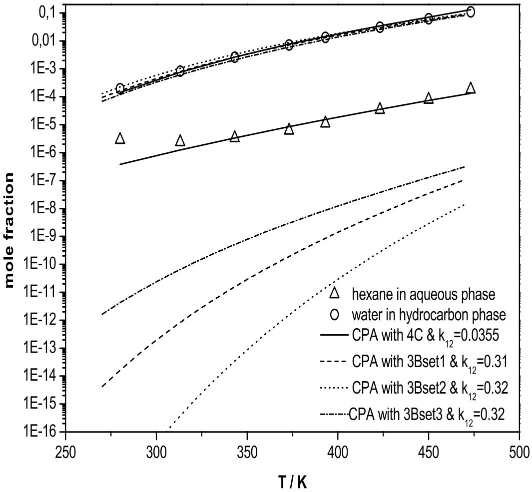


Figure 3.1. LLE correlation results for the system water – hexane using the 4C scheme and different sets for the 3B parameters. The parameters are shown in table 3.1. Experimental data are taken from Tsonopoulos & Wilson[18].

3.3. The association scheme of alcohols – Self associating binary systems

The 3B association scheme for alcohols (two sites in the 2 lone pairs of oxygen and one positive site for hydrogen) is consistent with the 4C scheme adopted for water and moreover is supported theoretically by a number of investigations with the SAFT model[19-23]. Moreover, investigations by

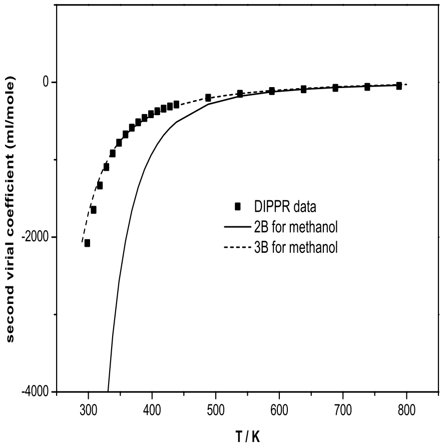
Wolbach and Sandler[24-26] based on SAFT and ab-initio methods have showed that 3B performs better than 2B for methanol.

Initially n-alcohols from methanol to n-octanol have been considered. The optimized pure compound parameters for n-alcohols using the 3B association scheme are presented in table 3.2. The pure compound parameters for n-alcohols with the 2B association scheme are tabulated in chapter 1; overall both association schemes fit equally well the experimental vapor pressure and liquid density data of pure components. As discussed by Kontogeorgis et al.[27], the physical significance of the pure component parameters of the CPA EoS can be independently tested. The value of the association energy ε^{AB} is related to the hydrogen bonding enthalpy. For methanol with the 2B association scheme the value of the association energy is 2958K while with the 3B scheme the value of ε^{AB} is 1932K; both values are close to the experimental range[27] which is 1700 – 2630K. For ethanol, hydrogen bonding enthalpy is reported experimentally[28] to be 2526 – 3007 K, which is in good agreement with the value 2590 K reported in chapter 1 with the 2B association scheme; the value with the 3B association scheme is somewhat smaller than the experimental one (1804K). For higher alcohols experimental values are not reported to the best of our knowledge.

Table 3.2. CPA parameters for n-alcohols with the 3B association scheme for T_r=0.55 – 0.90. T_c is presented in table 1.4

Compound	a_0 **(bar l^2 mol^{-2})**	b **(l/mol)**	c_1	ε^{AB} **(bar l mol^{-1})**	β^{AB} ***10^3**	**ΔP (%)**	**Δρ (%)**
methanol	4.598	0.0344	1.0068	160.70	34.4	0.4	0.5
ethanol	8.576	0.0500	1.0564	150.00	17.3	1.0	0.4
propanol	12.758	0.0655	0.9857	171.49	6.3	0.1	0.5
1-butanol	17.167	0.0814	0.8681	201.91	2.9	0.2	0.6
1-pentanol	22.728	0.0979	0.9807	180.12	3.4	0.2	0.5
1-octanol	41.900	0.1489	1.055	250.00	0.2	0.4	0.5

The performance of the pure component parameters can be further evaluated in terms of virial coefficients. It is well known that virial coefficients are directly related to intermolecular forces and a reasonable representation of virial coefficients from an equation of state suggests that the model correctly accounts for the physical interactions between the molecules. Experimental and calculated second virial coefficients for methanol and ethanol using the 2B and the 3B association scheme are presented in figures 3.2 and 3.3, respectively. For methanol the predicted second virial coefficients are much more accurate with the 3B scheme compared to the 2B. Opposite results are obtained for ethanol, where the predicted second virial coefficients with the 2B scheme are superior compared to the 3B.



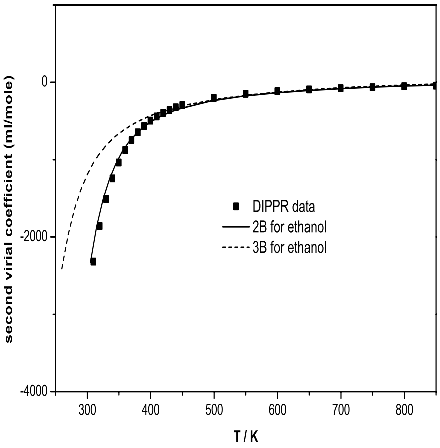


Figure 3.2. Prediction of second Virial coefficients for methanol. Experimental data are taken from DIPPR[66].

Figure 3.3. Prediction of second Virial coefficients for ethanol. Experimental data are taken from DIPPR[66].

One reason to attribute this behavior is the selected pure compound parameters. There are several sets of five parameters which can equally well fit experimental vapor pressure and liquid density data for the pure compounds. Hence it might be the case that other sets of pure compound parameters could equally well predict second virial coefficients with both association schemes. However the suggested parameters for alcohols with the two different association schemes have been carefully selected in order to accurately correlate the phase equilibria of alcohol – HC systems. The prediction of the second virial coefficients is an additional test of the performance of the model with the chosen set of parameters.

As mentioned previously, the suggested pure component parameters are chosen using as a criterion the accurate correlation of phase equilibria (LLE, VLE or SLE) of binary systems of alcohols with hydrocarbons. When the parameters are tested for phase equilibria calculations with hydrocarbons the influence of the combining rules is eliminated, since hydrocarbons are inert components and only self – association is allowed. The type of available equilibrium data is also dominant for the various optimal sets of possible pure component parameters (small deviations and similar accuracy in vapor pressures and liquid densities). If liquid-liquid equilibrium (LLE) data are available for the associating compound with an alkane, then such data could be used as “guide” for selecting the best set of pure compound parameters, among the various optimum sets (small deviations and similar accuracy in vapor pressures and liquid densities). This does not mean that the LLE data should be directly included in the parameter estimation, but can be used for screening among the best pure compound parameter sets. Typically by following this procedure a single set of optimum pure component parameters is obtained. For completely miscible alcohol-alkane systems, the final selection of pure alcohol parameters may be more difficult. In this case several sets of pure component parameters could provide equally good results, both in terms of VLE deviations for alcohol – alkane binary systems as well as vapor pressure and liquid density correlations of the pure alcohols. In such cases the performance of the parameters over extended temperature and pressure ranges should be considered, using both VLE and SLE data if possible. Occasionally LLE data for cross – associating alcohol – water systems might be considered, in order to further decrease the number of optimum sets of pure compound parameters.

Following the aforementioned procedure, the suggested pure component parameters for methanol and ethanol not only provide small vapor pressure and liquid density errors, but also correlate very adequate the LLE of several alcohol – hydrocarbon systems. Table 3.3 summarizes the LLE of the binary systems investigated, while typical results are presented in figures 3.4 – 3.7. Pure component parameters for hydrocarbons are already presented in chapter 1. CPA using a temperature independent binary interaction parameter can satisfactorily correlate LLE both with the 2B as well as with the 3B association scheme over an extended temperature range. For four binary systems, namely methanol – hexane, methanol – heptane, methanol – cyclohexane and methanol – octane isopiestic VLE data at atmospheric pressure are also available. For these systems the model is able to describe different types of phase equilibria using the same binary interaction parameter obtained from LLE data, as typically presented in figures 3.4 and 3.5 for the systems methanol – hexane and methanol – heptane, respectively. Even if overall the performance of the two different association schemes is similar, especially regarding the LLE, the 3B association scheme underestimates the vapor pressure of the system in the hydrocarbon rich area, as can be seen from the Txy diagram of figure 3.19. A detailed discussion for this behavior is provided in section 3.3.2. Very similar and in both cases satisfactory LLE results are obtained also for the other binary systems presented in table 3.3. Exception is the LLE of the systems methanol – nonane, methanol – decane and methanol – pentane (at an elevated however pressure of 50bar) where the performance of the 2B association scheme is superior to the 3B. The LLE correlation of methanol - decane system is presented in figure 3.7. Very similar is the correlation of methanol – nonane system.

An interesting observation is that the binary interaction parameter required for the LLE of alcohols with n-alkanes seems to be constant when the 3B association scheme is used. Even though the values reported in table 3.3 are the optimized ones, a value of k_{12}=-0.037 might be used for methanol – n-alkane and k_{12}=-0.051 for ethanol – n-alkane LLE, since the model using the 3B association scheme is not very sensitive to the k_{12}. Considering the temperature ranges presented in table 3.3, it is concluded that these k_{12} values provide very adequate results over extended temperature ranges. Unfortunately the lack of experimental LLE data for other low alcohol – alkane systems does not allow a more systematic study of this observation.

Table 3.3. Values of binary interaction parameters for the LLE of alcohol – alkane binary systems considered in this work.

System	**Ref**	**T min/ max [K]**	**k_{12} with 3B**	**k_{12} with 2B**
Methanol – pentane	29	272 – 289	-0.036 (50 bar)	0.0132 (50 bar)
Methanol – hexane	30, 33	245 – 307	-0.036	0.01
Methanol – cyclohexane	31, 32	275 – 318	0.012	0.04
Methanol – heptane	33, 34	278 – 323	-0.037	0.005
Methanol – octane	34	298 – 333	-0.037	0.0
Methanol – nonane	34, 70	298 – 353	-0.037	-0.006
Methanol – decane	34, 36,70	277 – 364	-0.037	-0.01
Ethanol – dodecane	35	271 – 286	-0.051	-0.031
Ethanol – tetradecane	35, 36	280 – 308	-0.051	-0.033
Ethanol – hexadecane	35, 36	290 – 327	-0.052	-0.04

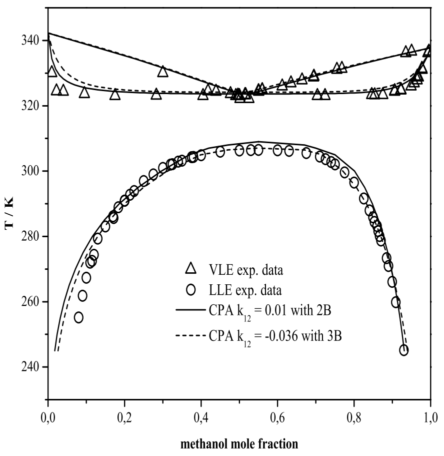


Figure 3.4. VLE and LLE correlation of methanol-hexane using the 2B or the 3B scheme for methanol. Exp. data from 30,33.

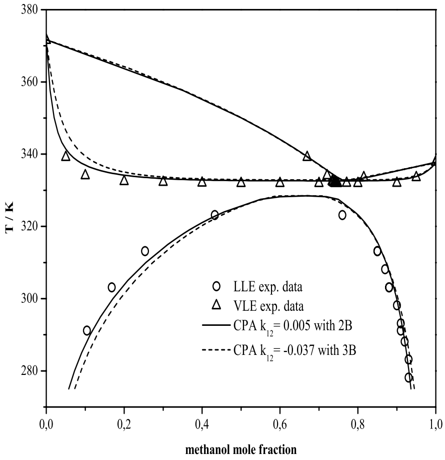


Figure 3.5. VLE and LLE correlation of methanol-heptane using the 2B or the 3B scheme for methanol. Exp. data from 33, 34.

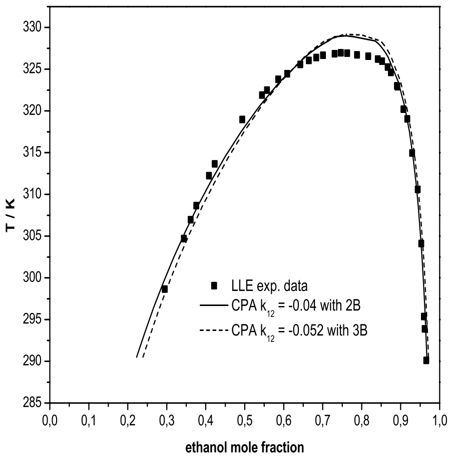


Figure 3.6. LLE correlation of ethanol-hexadecane using the 2B or the 3B scheme for ethanol. Exp. data from 35, 36.

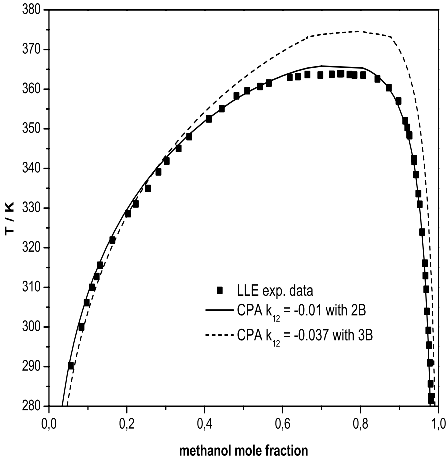


Figure 3.7. LLE correlation of methanol-decane using the 2B or the 3B scheme for methanol. Exp. data from 34, 36,70.

The VLE performance with the two association schemes is also considered. VLE correlation results of several alcohol – alkane binary systems are presented in table 3.4. A temperature independent binary interaction parameter is used to correlate different isotherms, if possible. The suggested temperature independent binary interaction parameter is optimized using all experimental data of different isotherms, or extrapolated from an isotherm with a large number of data points to lower or higher T in case of lack of data over the whole concentration range. For convenience, the optimized value of the binary interaction parameter per isotherm is also presented.

Several of the systems considered in this work form azeotropes, and the performance of the two association schemes was further evaluated based on the experimental and calculated azeotrope. It is concluded, that the performance of the two association schemes is, in general, very similar. No difference can be found when the azeotrope is formed at intermediate concentrations, or in the alcohol rich area. For example, for the system methanol – pentane[40] the azeotrope at 372.7K is formed at 0.348 of methanol mole fraction and 8.46bar. The calculated azeotrope with the 2B scheme for methanol and an optimized k_{12} at the isotherm (as tabulated in table 3.4) is at 0.384 of methanol mole fraction and 8.35bar while when the 3B scheme is used the azeotrope is formed at 0.382 of methanol mole fraction and 8.24bar. However, when the azeotrope is formed in the hydrocarbon rich area, the calculations with the 2B scheme are superior, even at elevated temperatures. For example the azeotrope for ethanol – isobutane[42] system at 363K is formed at 0.024 of ethanol mole fraction. With the 2B association scheme for ethanol the azeotrope is found at 0.014 of ethanol mole fraction, while when the 3B scheme is used the azeotrope is found at 0.005 of ethanol mole fraction. At lower temperatures, as for example 308.6K no formation of azeotropic is found with the 3B scheme.

Table 3.4. VLE correlation results and interaction parameters of alcohol – hydrocarbon systems. The optimum k_{12} per isotherm is also presented in parenthesis.

				3B			2B	
System	**Ref**	**T (K)**	**k_{12}**	**ΔP %**	**Δy*100**	**k_{12}**	**ΔP %**	**Δy*100**
methanol – propane	1	293.05	-0.029	3.9	1.5	0.026	3.1	1.3
	37	313.1	-0.012	8.6	0.5	0.059	4.3	0.8
	38	352.2	0.0	7.2	0.8	0.067	5.0	1.0
methanol - butane	39	273.15	-0.015	5.8	2.1	0.035	4.7	2.3
	39	323.15	0.0	2.8	0.8	0.050	1.3	0.8
	39	373.15	0.018	2.0	1.0	0.059	1.9	0.7
methanol – pentane	40	372.7	0.011	2.9	1.9	0.051	2.0	1.8

			(0.011)	(2.9)	(1.9)	(0.051)	(2.0)	(1.8)
	40	397.7	0.011	3.1	1.9	0.051	1.9	1.8
			(0.17)	(2.9)	(1.8)	(0.053)	(1.8)	(1.8)
	40	422.6	0.011	3.8	1.7	0.051	2.5	1.3
			(0.025)	(3.3)	(1.9)	(0.056)	(2.4)	(1.2)
ethanol – propane	41	325	0.019	3.2	0.3	0.038	3.2	0.2
			(0.017)	(3.0)	(0.3)	(0.037)	(3.2)	(0.2)
	41	350	0.019	3.4	0.4	0.038	3.2	0.3
			(0.012)	(2.3)	(0.5)	(0.031)	(2.2)	(0.5)
	41	375	0.019	6.7	0.8	0.038	5.6	0.9
			(0.035)	(5.8)	(0.9)	(0.053)	(5.1)	(1.0)
ethanol – isobutane	42	308.6	0.0	2.7	0.5	0.018	1.8	0.4
			(-0.01)	(1.7)	(0.4)	(0.010)	(1.7)	(0.4)
	42	318.4	0.0	2.3	0.9	0.018	1.6	0.8
			(0.0)	(2.3)	(0.9)	(0.017)	(1.6)	(0.8)
	42	363.5	0.0	4.9	3.5	0.018	4.0	3.4
			(0.018)	(2.7)	(3.0)	(0.036)	(1.9)	(2.9)
ethanol - pentane	43	372.7	0.034	3.2	1.6	0.045	2.4	1.2
			(0.024)	(3.0)	(1.5)	(0.037)	(2.3)	(1.2)
	43	397.7	0.034	2.5	1.0	0.045	2.1	1.1
			(0.034)	(2.5)	(1.0)	(0.046)	(2.1)	(1.1)
	43	422.6	0.034	2.5	0.9	0.045	2.1	0.7
			(0.033)	(2.5)	(0.9)	(0.049)	(2.0)	(0.7)
ethanol – hexane	44	298.15	0.0	2.4	1.4	0.01	1.2	0.5
ethanol – cyclohexane	45	298.15	0.022	3.6	2.9	0.033	2.7	2.1
			(0.022)	(3.6)	(2.9)	(0.033)	(2.7)	(2.1)
	45	323.15	0.022	3.8	1.7	0.033	3.3	1.5
			(0.033)	(1.6)	(1.5)	(0.044)	(1.2)	(1.1)
ethanol - heptane	48	303.15	-0.009	2.4	2.0	0.006	1.8	1.4
			(-0.009)	(2.4)	(2.0)	(0.006)	(1.8)	(1.4)
	48	313.15	-0.009	5.0	2.8	0.006	3.4	2.1
			(-0.009)	(5.0)	(2.8)	(0.006)	(3.4)	(2.1)
ethanol – isooctane	47	298.15	-0.036	2.6	2.0	-0.017	2.0	1.2
			(-0.036)	(2.6)	(2.0)	(-0.015)	(1.9)	(1.2)
	47	323.15	-0.036	6.0	4.1	-0.017	4.6	3.0
			(-0.023)	(5.8)	(4.2)	(-0.005)	(4.3)	(3.0)
propanol - hexane	48	298.15	0.006	1.5	0.3	0.017	1.0	0.3
			(0.006)	(1.5)	(0.3)	(0.017)	(1.0)	(0.3)
	48	323.15	0.006	2.0	0.7	0.017	1.6	0.6
			(0.006)	(2.0)	(0.7)	(0.017)	(1.6)	(0.6)
propanol - cyclohexane	49	298.15	0.023	0.8	0.6	0.029	1.0	0.6
1-butanol – hexane	50	298.15	0.005	3.4	0.6	0.012	4.1	0.6
			(0.002)	(3.0)	(0.6)	(0.007)	(2.9)	(0.8)
	51	323.15	0.005	2.2	0.3	0.012	2.5	0.4
			(0.005)	(2.2)	(0.3)	(0.012)	(2.5)	(0.4)
	52	333.15	0.005	3.4	0.4	0.012	3.5	0.4
			(0.014)	(1.2)	(0.2)	(0.021)	(1.4)	(0.2)
1-butanol – octane	53	283.16	0.0	2.8	-	0.0	1.4	-

			(-0.005)	(1.6)	-	(0.0)	(1.4)	-
	53	293.19	0.0	0.8	-	0.0	1.6	-
			(-0.001)	(0.6)	-	(0.003)	(0.9)	-
	53	298.15	0.0	0.5	-	0.0	2.4	-
			(0.0)	(0.5)	-	(0.007)	(0.7)	-
	53	308.09	0.0	1.5	-	0.0	3.0	-
			(0.003)	(0.7)	-	(0.01)	(1.0)	-
1-butanol – decane	54	358.15	0.0	1.2	0.9	0.015	0.9	0.6
			(0.007)	(1.1)	(0.9)	(0.013)	(0.8)	(0.6)
	54	373.15	0.0	1.6	0.5	0.015	0.8	0.3
			(0.009)	(1.0)	(0.4)	(0.015)	(0.8)	(0.3)
	54	388.15	0.0	1.8	0.6	0.015	1.0	0.3
			(0.011)	(0.7)	(0.4)	(0.016)	(1.1)	(0.3)
1-pentanol – heptane	55	358.15	0.018	2.4	1.0	0.024	2.3	1.1
1-octanol – decane	56	373.15	0.023	3.4	-	0.033	3.9	-
			(0.017)	(3.3)	-	(0.026)	(3.7)	-
	56	383.15	0.023	2.4	-	0.033	2.9	-
			(0.021)	(2.4)	-	(0.034)	(2.7)	-
	57	393.15	0.023	2.5	-	0.033	2.9	-
			(0.023)	(2.5)	-	(0.033)	(2.9)	-
	57	413.15	0.023	2.3	-	0.033	2.7	-
			(0.029)	1.3	-	(0.038)	(1.7)	-
1-octanol – undecane	57	393.15	0.03	1.6	-	0.04	2.0	-
			(0.03)	(1.6)	-	(0.04)	(2.0)	-
	57	413.15	0.03	1.9	-	0.04	2.3	-
			(0.035)	(1.4)	-	(0.045)	(1.6)	-
1-octanol – dodecane	57	393.15	0.03	1.1	-	0.04	1.3	-
			(0.027)	(0.7)	-	(0.037)	1.0	-
	57	413.15	0.03	1.2	-	0.04	1.7	-
			(0.032)	(0.8)	-	(0.044)	1.1	-
Average				**3.0**	**1.2**		**2.5**	**1.0**

The performance of the two different association schemes is further tested for SLE of some alcohol – alkane systems, for which experimental data were available. Table 3.5 summarizes the predictive and correlative performance of the association schemes. It is evident that the good in-built temperature dependence of the model (which is the actual property tested), both in the physical and the association term, is not influenced by the association scheme for the systems studied. The value of the binary interaction parameter required for the correlation of the systems is very small, and even the prediction is good (i.e. k_{12}=0.0) in both cases. Table 3.6 presents the calorimetric data used for the SLE calculations.

As a general conclusion, both association schemes provide overall similar VLE and SLE correlation results. Typical VLE correlation results are presented in figures 3.8 and 3.9 for the systems butanol – hexane and methanol – butane, respectively. For the system butanol – hexane a common temperature independent binary interaction parameter is used, providing very similar results with the two schemes. The use of a binary interaction parameter, fitted per isotherm, would improve the results, as shown in table 3.4. Finally, figure 3.10 presents the SLE of octanol – tetradecane system using both association schemes and a temperature independent binary interaction parameter, as presented in table 3.5. Accurate calculations are possible over a temperature range of 40K. The necessity of accounting for the non-ideality in the liquid phase is obvious, since the ideal behavior curve provides very poor results for the SLE of the system. Similar is the correlative performance of CPA for the rest of the systems studied.

Table 3.5. SLE prediction and correlation results of alcohol – hydrocarbon systems using the 2B and the 3B schemes for alcohols. $AAD = \frac{1}{NP}\sum\left|T_{\exp} - T_{cal}\right|$

		3B			2B		
System	**Ref**	**AAD [K] (k_{12}=0)**	**k_{12}**	**AAD [K]**	**AAD [K] (k_{12}=0)**	**k_{12}**	**AAD [K]**
1-butanol – octane	58	1.7	-0.004	0.9	1.9	-0.004	0.9
1-butanol – decane	58	3.9	-0.005	2.0	3.8	-0.005	1.9
1-octanol – octane	59	3.2	-0.008	2.3	2.2	-0.007	2.0
1-octanol – decane	56	0.6	-0.003	0.5	0.4	-0.002	0.3
1-octanol – undecane	60	0.3	-0.002	0.2	0.4	-0.003	0.2
1-octanol – dodecane	60	0.5	-0.007	0.2	0.3	-0.004	0.2
1-octanol – tetradecane	61	1.0	-0.005	0.2	0.3	-0.003	0.2
1-octanol – hexadecane	60	3.2	-0.008	1.1	2.9	-0.006	1.6
Average		**1.8**		**0.9**	**1.5**		**0.9**

As is the case for VLE, the performance of classical cubic EoS is not satisfactory for SLE of alcohol – alkanes. SRK EoS using the van der Waals one fluid mixing rules and a single interaction parameter cannot correlate the highly non ideal alcohol-alkane SLE, as can be seen in figure 3.11. The SLE of those systems significantly deviates from the ideal behavior (dot line in figure 3.10), as a result of the pronounced hydrogen bonding effects at low temperatures, which cannot be taken into account by the classical EoS.

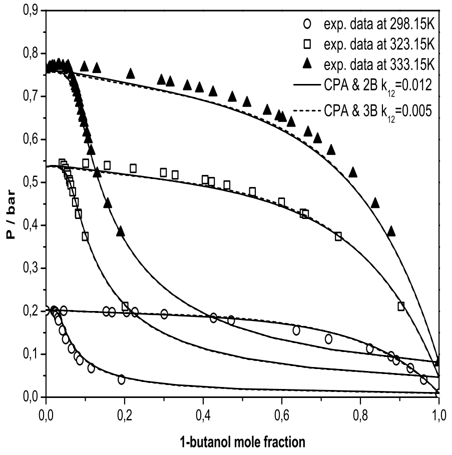


Figure 3.8. VLE of 1-butanol – hexane using a single T-independent interaction parameter. Exp. data from 50, 51 and 52.

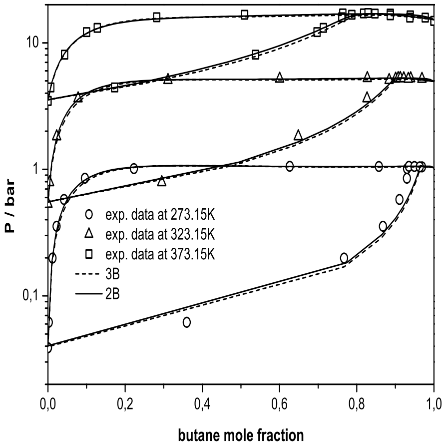


Figure 3.9. VLE for methanol – butane from 0–100 °C. The k_{12} per isotherm is shown in table 3.4. Exp. data from Leu et al.[39]

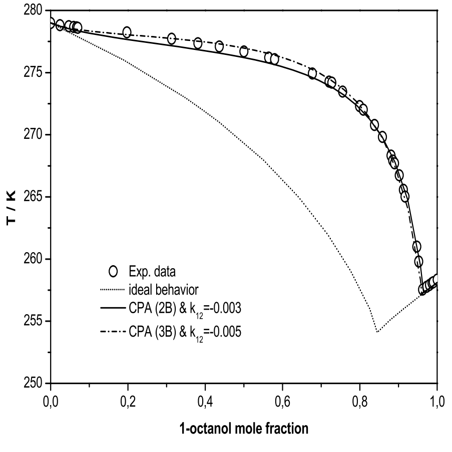


Figure 3.10. SLE correlation of n-octanol – tetradecane at 1 bar with the 3B and the 2B scheme. Exp. data are taken from Liu et al.[61].

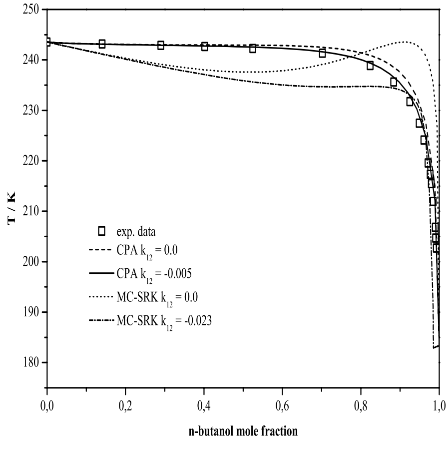


Figure 3.11. SLE prediction and correlation results with CPA and MC-SRK for n-butanol (2B) – decane system. Exp. data are taken from Plesnar [58].

3.3.1. High pressure SLE and LLE

The results presented so far for alcohol – hydrocarbon binary systems cover an extended temperature range while the overall performance of the two association schemes is very similar for the systems tested. The performance, however, of CPA over extended pressure ranges has not been tested previously, and only some VLE results for alcohol – water binary systems were presented in chapter 2, using the 2B association scheme for alcohols. Similar calculations will be further presented using the 3B scheme for alcohols. This section however focuses on high pressure applications of alcohol – alkane systems. For systems with only one associating component, the association schemes can be independently tested, since the performance is not influenced by the use of a combining rule, as is the case for cross – associating systems.

As a first application, high-pressure solid-liquid equilibria (SLE) for alcohol-hydrocarbons is presented, one of the very few types of associating mixtures for which such data is avalable. The working equation of SLE at low pressures is, assuming complete immiscibility in the solid phase and real solution behavior in the liquid phase[62]:

$$x_i \gamma_i = \exp\left[\frac{\Delta \mathrm{H}_i^{fus}}{RT_{mi}}(1-\frac{T_{mi}}{T}) + \frac{\Delta Cp_i}{R}(\frac{T_{mi}}{T} - 1 - \ln\frac{T_{mi}}{T}) \right] \tag{3.1}$$

This equation can be extended to high pressures, accounting for the pressure dependence of the enthalpy of fusion[63]. Assuming that the change in heat capacity as well as the specific molar volume of the pure liquid and solid are pressure independent, and that the solid is pure, the final equation for SLE calculations over the entire pressure range is:

$$x_i \gamma_i = \exp\left[\frac{\Delta \mathrm{H}_i^{fus}}{RT_{mi}}(1-\frac{T_{mi}}{T}) + \frac{\Delta Cp_i}{R}(\frac{T_{mi}}{T} - 1 - \ln\frac{T_{mi}}{T}) - \frac{(v_{0i}^S - v_{0i}^L)(P^+ - P)}{RT} \right] \tag{3.2}$$

The activity coefficient of the component i in the liquid phase is being calculated by CPA, while all the other parameters, namely the melting temperature $T_{m,i}$, the heat of fusion ΔH_i^{fus}, the specific solid molar volume v_{0i}^S and the specific liquid molar volume v_{0i}^L are obtained from experimental measurements at the standard pressure P^+ =1 bar.

There are only very few experimental SLE data at high pressures for mixtures containing associating compounds. In particular there are data available[64,65] for 1-octanol in mixtures with four n-alkanes (octane, dodecane, tetradecane and hexadecane). The calorimetric data for equation (3.2) are presented in Table 3.6. The specific solid molar volumes were adjusted to match the melting point data of pure compounds at various pressures. Liquid densities are obtained from DIPPR[66]. Although the solid volumes of table 3.6 are only about 2-3% higher than those of DIPPR, SLE calculations are rather sensitive to the thermophysical properties used for the pure compounds, thus a correct representation of pure compounds is crucial. A typical case is presented in figure 3.12 for the freezing temperature of n-octanol over an extended pressure range up to 1800bar. The dashed line presents the calculated freezing temperatures from eq. (3.2) with the solid volumes obtained from DIPPR while the solid line presents the results with fitted values of solid molar volumes. For pure compounds, the results are not influenced from the model used for the properties of the liquid phase.

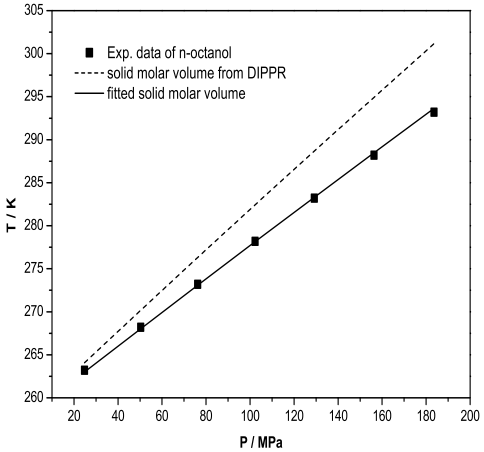


Figure 3.12. Calculated freezing temperatures of pure n-octanol over an extended pressure range. Experimental data are taken from Yang et al.[65]

Both prediction (k_{12}=0) and correlation of low pressure SLE is very satisfactory for these systems, as already summarized in table 3.5 using both association schemes. Figure 3.13 presents SLE calculations for the system octanol – dodecane at high pressures and for different values of octanol mole fraction. The k_{12} obtained from SLE data at atmospheric pressure is used. Even though only the performance of the 2B association scheme is presented, the results obtained with the 3B association scheme are very similar. CPA EoS provides very adequate correlation of the SLE of the system for pressures up to 1700 bar, for both low and very high mole fractions of octanol. For intermediate values of octanol mole fraction, the model tends to underestimate the freezing temperatures of the system by about 3K.

Table 3.6. Calorimetric data required for equation (3.1) for low pressure SLE and equation (3.2) for high pressure SLE. The values for v_{0i}^S are fitted to the pure component properties.

Component	**Ref**	$T_{m,i}$ **(K)**	ΔH_i^{fus} **(J/mol)**	v_{0i}^S **(l/mol)**	v_{0i}^L **(l/mol)**	ΔCp_i **J/mol.K)**
1-butanol	67	183.35	9282	-	-	-
1-octanol	56, 64	258.1	23700	0.134548	0.152859	41.33
n-octane	58, 68	216.52	20740	0.132565	0.150245	-
n-decane	56, 68	243.54	28700	-	-	-
n-undecane	60, 68	247.64	22180	-	-	-
n-dodecane	60, 68	263.46	36836	0.194394	0.221550	-
n-tetradecane	61, 68	278.99	45070	0.220056	0.256906	-
n-hexadecane	60, 64	291.54	51914	0.251120	0.292566	-

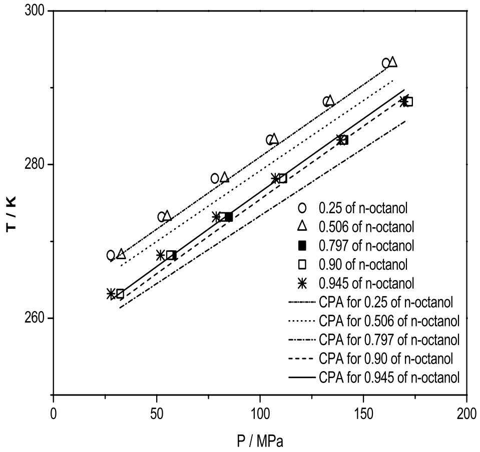


Figure 3.13. SLE correlation of n-octanol – dodecane system at high pressures using a value of an interaction parameter k_{12}=-0.004 obtained from SLE data at atmospheric pressure and the 2B association scheme for n-octanol. Experimental data are taken from Yang et al.[65]

Equally satisfactory results are obtained for the two other heavier alkanes with k_{12} values obtained from low presure SLE and the results for octanol-hexadecane are shown in figure 3.14. Only in the case of octanol-octane were the predictions at high pressures not entirely satisfactory using the k_{12} from low pressure data. Irespectively of the association scheme used for n-octanol, the model yields an underestimation of the freezing temperature of about 2K (high octanol concentrations) up to 9K (low octanol concentrations). The use of a different value of the binary interaction parameter (k_{12}=0.012 for 2B and k_{12}=0.011 for 3B) provides adequate results over the entire pressure range tested. Finally, figure 3.15 shows high pressure SLE results with CPA for octanol-tetradecane using the two different association schemes (i.e. 2B and 3B).

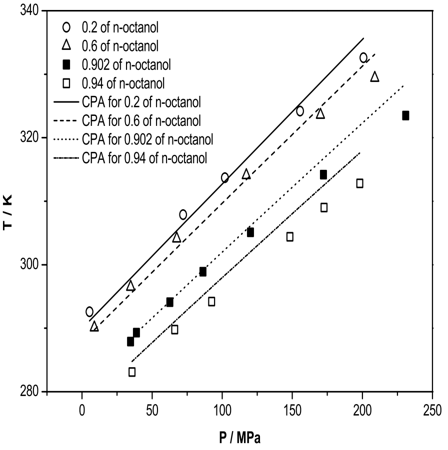


Figure 3.14. SLE correlation of n-octanol – hexadecane system at high pressures using a value of an interaction parameter k_{12}=-0.006 obtained from SLE data at atmospheric pressure and the 2B association scheme for n-octanol. Experimental data are taken from Yang et al.[64]

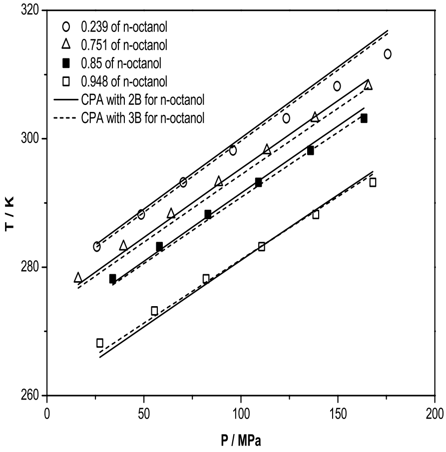


Figure 3.15. SLE correlation of octanol – tetradecane system at high pressures with the 3B scheme for octanol and an interaction parameter k_{12} = -0.005 obtained from SLE data at P = 1bar. The performance of the model with the 2B scheme for octanol and a binary interaction parameter k_{12} = -0.003 is also presented. Exp. data are taken from Yang et al.[64]

The second application considered in this section is high pressure LLE for alcohol – alkanes. Even though such experimental data are rare and unfortunately cover only a limited temperature range, useful conclusions might be drawn regarding the performance of the two association schemes. The binary systems considered are presented in table 3.7, together with the optimized k_{12} value of the 2B/3B association scheme per pressure. It was mentioned that in the case of low pressure LLE using the 3B association scheme, the performance of the model was not very sensitive to the k_{12} used. The correlation of high pressure LLE is by far more sensitive to the value of the binary interaction parameter used compared to the low pressure one irrespectively of the association scheme used. The use of the same value of k_{12} obtained from low pressure LLE cannot be used for high pressure LLE, as table 3.7 indicates; only in the case of methanol – hexane system the same binary interaction parameter (k_{12}=-0.036) can be used over the whole pressure range. The use of different k_{12} values for high pressure LLE was also reported by Yarrison and Chapman[69] for the PC-SAFT and CK-SAFT EoS.

It is observed that when the model performs adequately for low pressure LLE, then the same good performance is also experienced for high pressure LLE. Consequently, high pressure LLE are very similar with both association schemes for methanol – hexane, ethanol – tetradecane and ethanol – hexadecane, but the performance of the 2B association scheme is superior for methanol – pentane, methanol – nonane and methanol - decane, as it was found for low pressure LLE. Even though the limited temperature range of the available experimental high pressure LLE data, usually covering a temperature range of 20K, does not support a general statement, the results provide a good indication for the performance of the model with the two association schemes. Typical results for high pressure LLE of methanol – pentane are presented is figure 3.16. It was already mentioned in the previous section that 2B performs better at the lower pressure (50bar). The better performance of 2B is also experienced at higher pressures up to 800bar, as demonstrated by figure 3.16.

In this section high pressure SLE and LLE applications of alcohol – alkane systems were presented. As a result of the study of both high pressure SLE and LLE, the implementation of the rigorous 3B association scheme for alcohols provides no advantage over the simple 2B association scheme.

Table 3.7. High pressure LLE for alcohol – alkane systems. The k_{12} values for 2B/3B scheme are optimized for each pressure.

System	**Ref**	**50 bar**	**100 bar**	**400 bar**	**800 bar**
methanol – pentane	29	0.0132/-0.036		0.01/-0.032	0.007/-0.032
methanol – hexane	70		0.007/-0.036	0.004/-0.036	-0.001/-0.036
Methanol – nonane	70		-0.0098/-0.042	-0.0218/-0.0502	-0.034/-0.0578
methanol – decane	70		-0.0163/-0.0454	-0.0308/-0.0572	-0.044/-0.067
ethanol – tetradecane	35			-0.04/-0.057	-0.061/-0.06
ethanol – hexadecane	35			-0.0509/-0.068	-0.058/-0.074

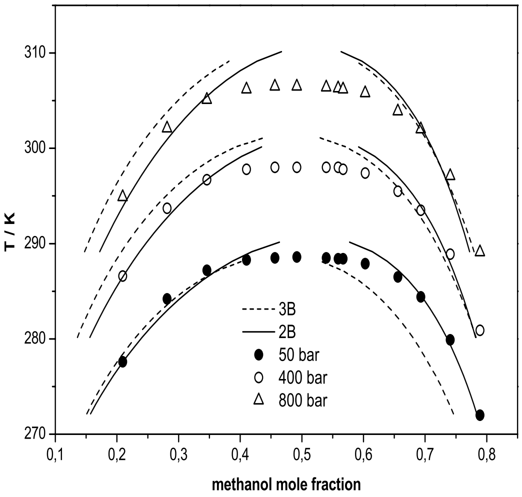


Figure 3.16. LLE correlation of methanol – pentane system at high pressures with CPA using the 2B and 3B scheme for methanol and optimum k_{12} parameters as presented in table 3.7. Experimental data are taken from Haarhans and Schneider[29].

3.3.2. Investigation of the influence of the association scheme in the behavior of the model.

As demonstrated in the previous section both association schemes tested for alcohols provide overall similar VLE, SLE and LLE results for alcohol – hydrocarbon mixtures. Nevertheless, by adding an extra site, the contribution of the association term in the model changes significantly. Figure 3.17 shows the net contribution of the physical terms of CPA (the SRK attractive and repulsive term) to the vapor pressure of pure ethanol as a function of temperature for the 2B and the 3B association schemes based on the pure component parameters of ethanol. With 2B the net contribution of the physical terms is larger than with 3B, and therefore requires a higher (negative) contribution for the association term, compared to 3B. A similar behavior is observed for the other alcohols as well; however, when the carbon chain is increased the difference in volatility decreases.

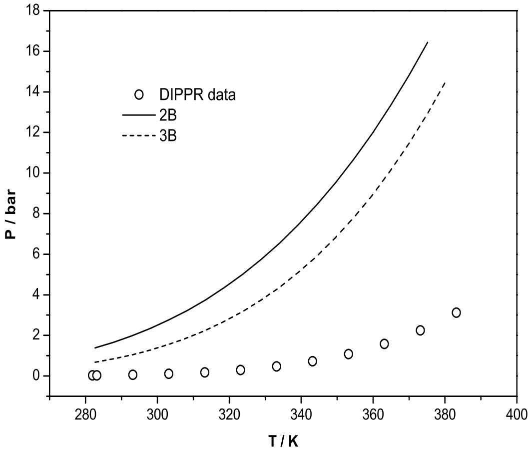


Figure 3.17. Performance of the physical term of CPA (i.e. repulsive and attractive term from the SRK – part) in the calculation of the vapor pressure of pure ethanol, using the 2B and 3B schemes.

These differences in the physical terms affect the behavior of the model at infinite dilution. Figure 3.18 presents calculated activity coefficients for the binary system of ethanol –cyclohexane at 298.15K, using the two different association schemes and the optimized values of the binary interaction parameter. The VLE correlation of the system is presented in figure 3.19. The calculated activity coefficients are overall similar (as the VLE is) in both cases. In the hydrocarbon rich area, however, the association forces are less pronounced. The total contribution of the physical term of CPA dominates the performance of the model at this end and higher values of infinite activity coefficients are seen with 2B. This is a typical behavior, systematically experienced in systems of lower alcohols with alkanes, especially for methanol and ethanol.

As a result, even when explicitly fitting binary interaction parameters per isotherm, the performance of the two schemes might be similar over the whole composition range but systematically superior with the 2B scheme in the hydrocarbon rich end. Such a behavior is not observed is the alcohol rich end, where when a binary interaction parameter is used, both schemes perform identical. Due to the superiority of the 2B association scheme in the hydrocarbon rich end, the VLE correlative performance is slightly but systematically better that the 3B, as table 3.4 demonstrates.

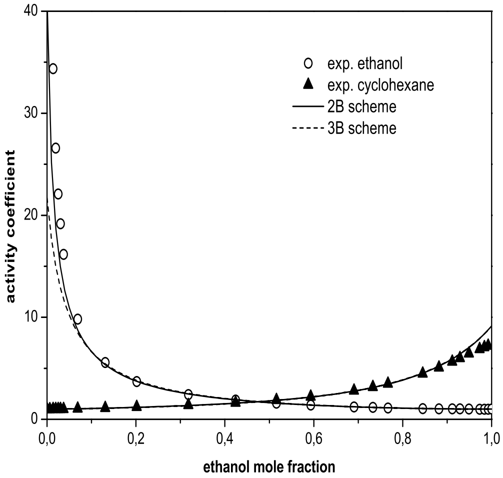


Figure 3.18. Experimental and calculated activity coefficients for the binary system of ethanol – cyclohexane at 298.15K, using the 2B and the 3B association scheme for ethanol. The binary interaction parameters used are k_{12}=0.033 for the 2B association scheme and k_{12}=0.022 for the 3B. The infinite dilution activity coefficient of ethanol with the 2B association scheme is $\gamma^{\infty} = 41$ while the value using the 3B scheme is almost half.

The values of the binary interaction parameters presented in table 3.4 clearly demonstrate that the 3B association scheme requires systematically lower values of the k_{12}. This might lead to the conclusion that the prediction with the 3B association scheme is superior compared to the 2B. This is, however, not the case, due to the fact that when the 3B association scheme is used, the model predicts in most cases (for binary systems of lower alcohols and especially in the presence of light alkanes) an incorrect phase split, even at elevated temperatures. This behavior is also experienced for systems of low alcohols with heavier alkanes, such as the system ethanol – iso-octane but only at low temperatures. Hence, the use of a binary interaction parameter is required in most of the cases when the 3B association scheme is used for low alcohols. Interestingly enough, when the 2B association scheme is used, no incorrect phase split is predicted (i.e. when k_{12}=0) for the systems presented in table 3.4, but the error in vapor pressure is in most of the cases high enough to require a binary interaction parameter as well.

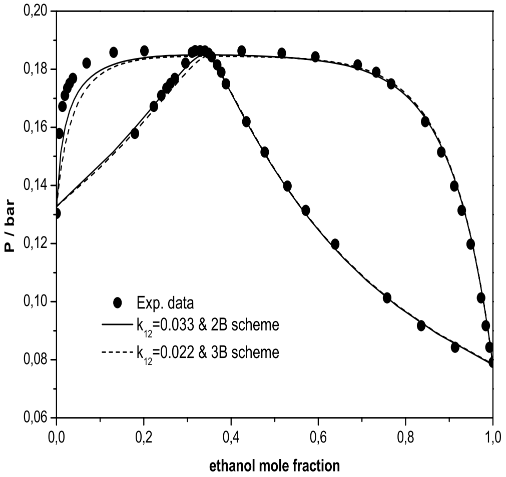


Figure 3.19. VLE correlation of ethanol – cyclohexane at 298.15K, using the 2B and the 3B association scheme for ethanol. Experimental data from Coto et al.[45]

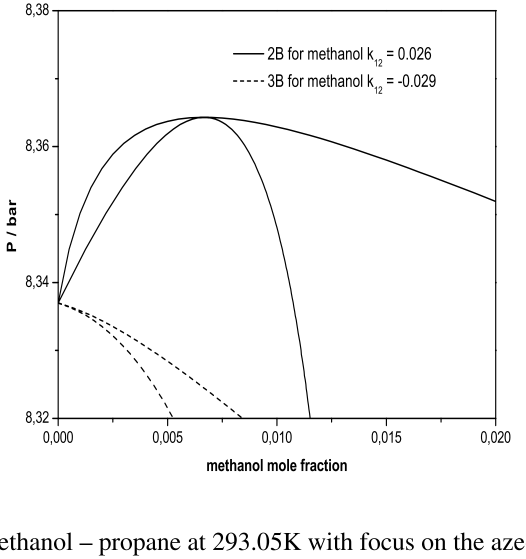


Figure 3.20. VLE for methanol – propane at 293.05K with focus on the azeotropic area.

However, a limitation of the 3B over the 2B scheme is revealed in the systematic study of the “sensitive very non-ideal” alcohol-alkane mixtures, especially vapor-liquid equilibria and high pressure LLE. It is already shown that 2B association scheme performs better for methanol –

pentane over the whole pressure range and that when the 2B scheme is used, the model performs better in the hydrocarbon rich end, both in terms of calculated bubble point pressure as well as azeotropic composition. A typical example is shown in figure 3.20 for methanol-propane where there is industrial evidence for the existence of azeotrope at low methanol concentrations[71]. Only CPA using the 2B scheme can predict this behavior (at about 0.6% methanol), as can be seen in figure 3.20.

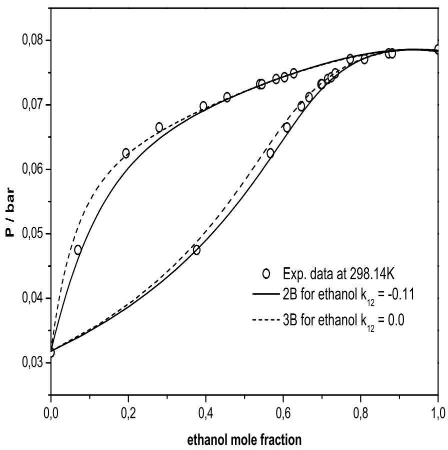
3.4. The association scheme of alcohols – Cross-associating binary systems of alcohols with water

As already mentioned, the implementation of the 3B association scheme is rigorously correct based on the chemical structure of alcohols. Another, and rather more important reason for implementing the 3B scheme for alcohols is because one additional active site in the molecule of alcohols is expected to increase the contribution of the cross-association strength for the binary water – alcohol systems and consequently decrease the high and negative values of the binary interaction parameters (k_{12}) in the physical term of the model, when the one fluid Van der Waals mixing rule is used.

The VLE correlation of n-alcohol – water systems with the 3B association scheme for alcohols is presented in table 3.8. As already discussed in chapter 2, CR-2, CR-3 and CR-4 combining rules not only provide inferior results compared to CR-1 or ECR, but also lack theoretical justification. Due to lack of theoretical justification, those combining rules are not considered in this study.

Evaluating the performance of the two different combining rules, when the 3B association scheme is used for n-alcohols, CPA with ECR performs superior compared to CR-1. Furthermore, as in the case of the 2B scheme, ECR with a temperature independent binary interaction parameter provides equally satisfactory results over extended temperature and pressure ranges for all binary systems tested; equally satisfactory results are achieved for the calculated azeotropes of ethanol – water system, as table 3.9 demonstrates.

What is however very important is the much lower value of the binary interaction parameter required for VLE calculations with ECR combining rule and the 3B scheme for n-alcohols. Starting from methanol – water system the 3B scheme requires a significantly lower k_{12} (0.035) compared to the 2B scheme (-0.09). Not only the k_{12} value is small but also positive, which indicates that the model describes better the physical interactions (i.e. cross – association) compared to the 2B and that the problem of underestimating the degree of solvation can be successfully approached by adding one more active site in the molecule of n-alcohols within the CPA framework. The results are even better for the binary water – ethanol and water – n-propanol systems, where no binary interaction parameter is required (i.e. pure prediction) for successful calculations with the 3B scheme. Typical VLE results for ethanol – water are presented in figure 3.21. The SLE of methanol – water can be also successfully modeled with ECR, but in this case a slightly different value of the binary interaction parameter should be used (k_{12}= -0.012) compared to VLE. CR-1 is also an alternative, as with the 2B scheme. For the intermediate complex phase the heat of fusion at the same reference temperature used in chapter 2 is 7345 J mol^{-1}, which is quite close to the optimized value of the heat of fusion when methanol is assumed to have two active sites (8540 J mol^{-1}). The SLE correlation of the system using the 3B and 2B schemes is presented in figure 3.22.



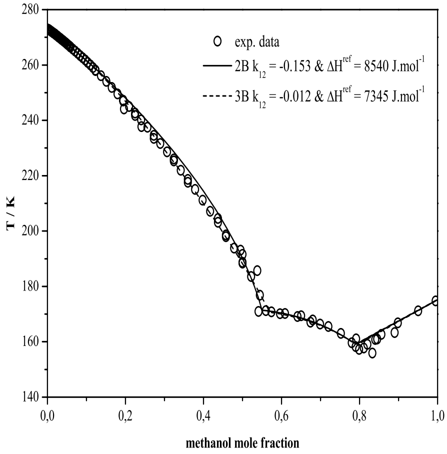


Figure 3.21. VLE of ethanol – water at 298.14K using the 2B and 3B scheme for ethanol. Exp. data from Phutela et al.[75]

Figure 3.22. SLE of methanol – water using the 2B and 3B scheme for methanol. Exp. data from Miller[86], Vuillard[87] and Ott[88].

Table 3.8. VLE correlation results for water – n-alcohols using the 3B schemes for alcohols with ECR or CR-1 combining rule and ECR with a temperature independent binary interaction parameter (*k_{12}*). The average error with the 2B scheme is also presented.

System	**Ref.**	**T (K)**	**CR-1**			**ECR**			**ECR common k_{12}**		
			k_{12}	**ΔP %**	**Δy * 100**	**k_{12}**	**ΔP %**	**Δy * 100**	**k_{12}**	**ΔP %**	**Δy * 100**
water – methanol	72	298.15	0.055	3.4	1.2	0.029	2.3	0.8	0.035	2.6	0.8
	73	333.15	0.095	1.5	1.1	0.055	0.6	0.7	0.035	2.9	1.1
	74	373.15	0.077	1.2	1.0	0.039	2.1	0.9	0.035	2.2	0.9
	74	423.15	0.096	0.8	0.7	0.053	0.7	0.9	0.035	1.3	1.0
	74	473.15	0.092	1.1	0.6	0.044	0.7	0.5	0.035	1.0	0.5
	74	523.15	0.088	1.5	1.5	0.032	0.8	1.2	0.035	0.8	1.2
water – ethanol	75	298.14	0.050	4.7	2.8	-0.028	0.3	0.6	0.0	0.9	0.9
	73	333.15	0.067	2.2	2.2	0.0	0.7	0.6	0.0	0.7	0.6
	76	343.15	0.051	3.2	2.1	-0.003	0.9	0.5	0.0	1.0	0.6
	76	363.15	0.056	2.8	2.1	-0.002	0.6	0.4	0.0	0.7	0.4
	77	423.15	0.059	1.5	1.5	-0.020	1.7	0.7	0.0	3.1	3.8
	77	473.15	0.049	1.6	1.2	-0.030	1.3	0.5	0.0	3.6	1.0
	77	523.15	0.048	2.6	0.9	-0.043	1.3	0.4	0.0	3.1	0.7
	77	598.15	-0.009	1.5	1.2	-0.097	1.7	1.3	0.0	3.1	2.7
	77	623.15	-0.056	1.6	2.0	-0.014	1.6	2.4	0.0	2.0	2.6
water – propanol	72	298.15	0.036	8.1	4.8	-0.015	2.9	1.5	0.0	3.7	2.1
	78	333.15	0.068	4.2	3.6	-0.012	0.6	0.8	0.0	1.0	1.2
	79	363.15	0.056	3.9	3.3	-0.025	0.8	0.6	0.0	2.3	0.9
water –butanol	72	298.15	0.044	14.7	6.3	-0.014	5.6	2.2	-0.017	5.4	2.0
	85	363.15	0.055	11.3	5.7	-0.014	1.6	0.9	-0.017	1.8	0.6
	85	383.15	0.056	10.6	5.3	-0.017	1.8	1.0	-0.017	1.8	1.0
	85	403.15	0.054	9.1	5.0	-0.026	1.4	1.1	-0.017	1.3	1.7
Average error				**3.3**	**2.2**		**1.2**	**0.8**		**1.9**	**1.1**
Average error (2B)				**2.4**	**1.6**		**1.7**	**0.8**		**2.1**	**1.3**

Table 3.9. Experimental and calculated azeotropic composition for ethanol (1) – water (2) system with ECR and a single binary interaction parameter k_{12}= -0.11 with the 2B or k_{12}= 0.0 with the 3B scheme for ethanol.

T (K)	**Ref**	**experimental**		**2B**		**3B**	
		x(1)	**P / bar**	**x(1), calc**	**P calc / bar**	**x(1), calc**	**P calc / bar**
333.15	73	0.91	0.4705	0.92	0.4780	0.932	0.4769
343.15	76	0.9092	*NA*	0.917	0.7384	0.925	0.7361
363.15	76	0.8845	*NA*	0.90	1.6144	0.898	1.608
523.15	77	0.756	71.7055	0.72	69.6788	0.78	70.225

NA: not available

In chapter 2 it was shown that CPA with the 2B scheme and CR-1 rule can satisfactorily correlate the LLE of water – higher alcohol binary systems with the use of a single binary interaction parameter. LLE calculations for three binary systems, namely water – n-butanol, water – n-pentanol and water – n-octanol are performed with the 3B scheme for n-alcohols, using both CR-1 and ECR rule. As mentioned in section 3.3 when the pure compound parameters for associating compounds are optimized based on vapor pressure and liquid density data, several sets of parameters can be obtained. In order to decrease the number of the optimum sets of pure component parameters, LLE data of cross – associating systems with water might be also considered. Such a procedure was followed for the proposed parameters of n-alcohols with both schemes. However, when the 3B scheme is implemented, it was not possible to obtain a set of parameters that provides satisfactory vapor pressure and liquid density results for the pure components and at the same time correlates both solubilities for water – n-alcohol systems. Figure 3.23 presents correlation results for n-octanol – water with the 3B scheme using CR-1 and ECR rule. For comparison reasons the performance of 2B scheme is also presented, using CR-1 and k_{12}=-0.059.

One reason to attribute this behavior is the pure component parameters of heavy n-alcohol with the 3B association scheme, especially considering the number of possible sets that equally well fit to experimental vapor pressure and liquid density data. Although this is an argument which is difficult to be eliminated, the concept of three active sites in the molecule of higher alcohols is questionable. Due to steric effects it is expected that alcohols with a long chain loose the bonding activity of at least one of their sites; as a consequence the assumption of three equally active sites might lead to a misinterpretation of the physical behavior which is pronounced in the case of LLE with water. The concept of the steric effects seems to be further supported by a recent investigation by Von Solms et al.[90]. The authors performed predictions of monomer fractions for methanol, ethanol, 1-propanol and 1-octanol using CPA with both 2B and 3B schemes and the pure component parameters presented in chapter 1 (for the 2B) or in table 3.2 for the 3B. They concluded that a three-site scheme is best only for methanol; two- or three-site schemes perform about equally for ethanol, but for higher alcohols a two-site scheme is preferred.

Summarizing the performance of the 3B association scheme for water - alcohol binary systems no advantage is gained in terms of correlation when compared to the 2B scheme, given that i) both association schemes perform equally well for VLE over extensive temperature and pressure range, ii) adequate calculations can be obtained for SLE of methanol – water with both association schemes iii) the use of different combining rules for different types of phase equilibria still remains an issue, especially when considering the inferior performance of CPA using the 3B scheme for n-alcohol – water LLE (figure 3.23).

A clear advantage when using the 3B scheme for alcohols is the significantly lower value of the binary interaction parameters required for the same good performance as with the 2B scheme. The low values of the binary interaction parameters (or even no need for interaction parameters) indicate that the physical picture of solvation is adequately described for the mixtures of low alcohols with water, in the case of which, the assumption of three active sites can be well justified.

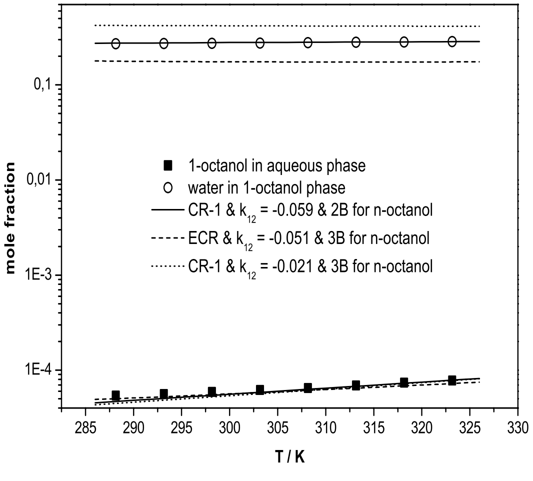


Figure 3.23. LLE of n-octanol – water using the 2B and 3B scheme for n-octanol. Exp. data from Dallos[89].

3.5. Multicomponent systems

A very demanding test and the final purpose for the development of a thermodynamic model is the ability to predict adequately multicomponent multiphase equilibria, based solely on binary interaction parameters. CPA using the 2B association scheme for alcohols and the 4C scheme for water is already shown[4,80] to provide satisfactory prediction of multicomponent multiphase equilibria of systems containing water, methanol or ethanol and hydrocarbons.

It has been already discussed that the major advantage of the 3B scheme for alcohols is the low value of the binary interaction parameters for binary mixtures with water. When a binary interaction parameter is used with the 2B scheme, however, the performance is very similar. The systematically inferior performance of the 3B scheme in the hydrocarbon rich area for alcohol – alkane mixtures, the inferior correlation of some binary methanol - alkane LLE, the false phase splits concerning VLE prediction of low alcohol – alkanes even at elevated temperatures are among the drawbacks of the 3B scheme.

In this section the predictive performance of CPA, based solely on the same binary interaction parameters, is tested for multicomponent alcohol – water – hydrocarbon systems at various conditions. For alcohol – water cross – associating systems, ECR with a common interaction parameter is used for both association schemes, in accordance to the results presented in chapter 2 and section 3.4. The use of the optimized binary interaction parameters for alcohol – water mixtures provides very similar results.

Three multicomponent systems containing methanol have been tested using the 2B and 3B schemes. The multicomponent systems considered are methanol – water – propane, methanol – water – butane and methanol – water – hexane, the first two of them at two different temperatures. Although the prediction of the methanol concentration in the polar phase is similar in most of the cases with both schemes, the results with the 2B scheme are superior regarding the predicted methanol concentration in the HC phase. The error for the methanol solubility in the hydrocarbon phase is half compared to that with the 3B scheme, probably due to the superior performance of the 2B scheme in the hydrocarbon rich end. Consequently, the prediction of methanol partition coefficient, which is of interest to the oil industry, is superior with the 2B scheme.

Typical results are presented in figure 3.24, which presents predictions of the partition coefficient of methanol between the hydrocarbon (HC) and the polar phase at 273.15K and 293.15K for the ternary system methanol – water – n-butane. The performance of the two different schemes, for the prediction of methanol partition coefficient, is similar for the other mixtures as well. Similar conclusions are also obtained for the prediction of the binodal curve for all the ternary systems with methanol, but only partition coefficients plots are presented. For the predictions of the multicomponent systems the following cases and binary interaction parameters are considered: Case 1 uses the 2B scheme for methanol, ECR rule with k_{12}=-0.09 for methanol – water system, the k_{23} is obtained from the correlative equation k_{ij}=*-0.026*(carbon number) + 0.1915* (for details see chapter 4) and k_{13}=0.026 for methanol - propane, k_{13}=0.035 for methanol - butane and k_{13}=0.01 for methanol - hexane. Case 2 uses the 3B scheme, ECR rule with k_{12}=0.035 for methanol – water system, the k_{23} is obtained as in case 1 and k_{13}=-0.029 for methanol - propane, k_{13}=-0.015 for methanol - butane and k_{13}=-0.036 for methanol - hexane. Case 3 is similar to case 1 but k_{23} is set to zero (this case is discussed further in section 3.6).

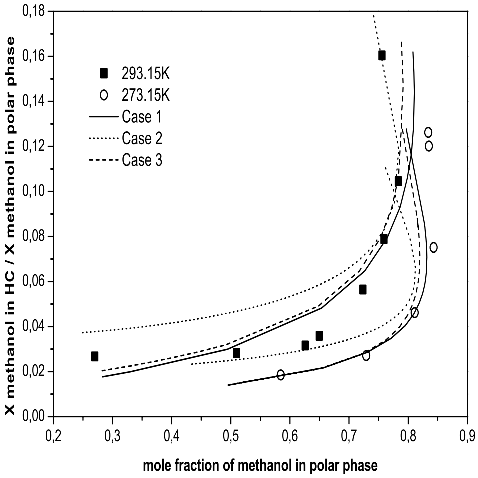


Figure 3.24. Prediction of the partition coefficient of methanol between the hydrocarbon (HC) and the polar phase for the ternary system of methanol (1) – water (2) – n-butane (3) at 273.15K and 293.15K. The three different cases are: Case 1: k_{12} = -0.09 (ECR), k_{13} = 0.035 and k_{23} = 0.0875 and 2B scheme for methanol, (solid line) Case 2: k_{12} = 0.035 (ECR), k_{13} = -0.015 and k_{23} = 0.0875 and 3B scheme for methanol, (dot line) Case 3: k_{12} = -0.09 (ECR), k_{13} = 0.035 and k_{23} = 0.0 and 2B scheme for methanol, (dash line). Experimental data are taken from Noda et al.[81].

Figure 3.25 and 3.26 present prediction results for the solubility of methanol in the polar and hydrocarbon phase versus the water mole fraction in the polar phase for the ternary systems water –

methanol – propane and water – methanol – hexane, respectively. As already mentioned, the predicted solubility of methanol in the hydrocarbon phase is systematically in higher error with the 3B scheme, compared to the 2B. A similar behavior is concluded for the hydrocarbon solubility in the polar phase, where once again predictions with the 2B scheme for methanol are superior. Finally the water solubility is similarly predicted with both schemes (i.e. case 1 and case 2).

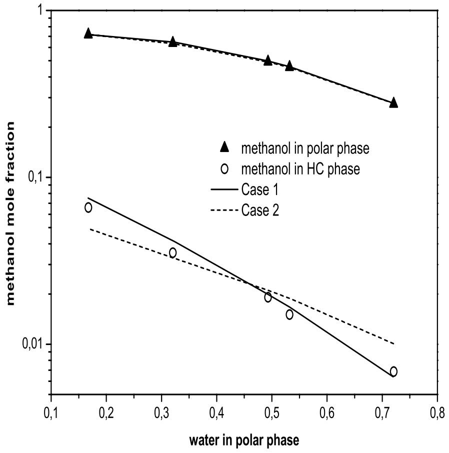


Figure 3.25. Prediction of methanol solubility in the polar and HC phase for methanol – water – propane at 293.1K. Exp. data from Noda et al.[81].

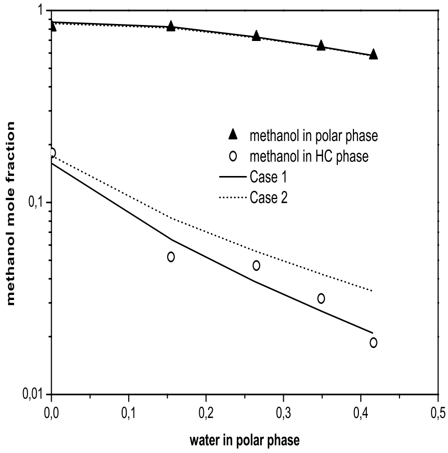


Figure 3.26. Prediction of methanol solubility in the polar and HC phase for methanol – water – hexane at 293.1K. Exp. data from Kogan et al.[82].

Two multicomponent systems containing ethanol are considered as well, namely ethanol – water – hexane and ethanol – water – heptane and it is concluded that the predictive performance with both schemes is very similar. As figure 3.27 illustrates, the prediction of the partition coefficient of ethanol is satisfactory using both association schemes. Successful results are also obtained for the binodal curve prediction of the system with both schemes.

Methanol with the 3B association scheme provides inferior predictions of multicomponent systems. Methanol is a very important component in the oil and gas industry, since it is used extensively as gas hydrate inhibitor, and the correct prediction of the distribution of methanol among the various phases is a key property for successful applications. The inferior performance of the 3B scheme for systems with methanol is probably related to the reasons already discussed in section 3.3.2., which are being pronounced in the case of the ternary systems. On the other hand, the 2B scheme is found to be successful for phase equilibria calculations both for binary and ternary systems. The use of the high binary interaction parameter with the 2B scheme might be a drawback from the physical point of view, but within an engineering framework not only provides satisfactory VLE, LLE and SLE results for binary systems, both at low and high pressures and over extended temperature ranges, but also satisfactory predictions of multicomponent systems. These conclusions are also valid, besides methanol, for the other alcohols tested with the 2B association scheme. Considering CPA as a model for applications within a broader engineering framework, and using an anyhow semi-empirical approach in order to account for the physical interactions (SRK term), we find as yet to reason to implement the 3B scheme for alcohols.

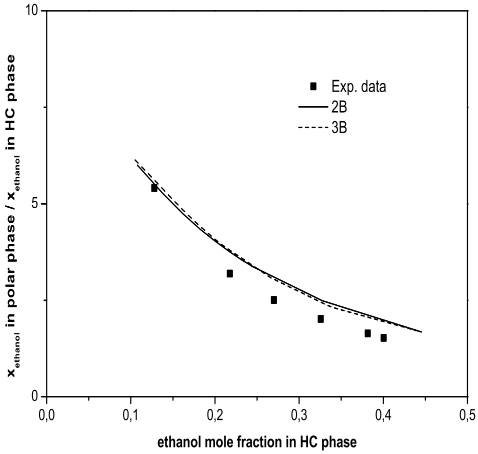


Figure 3.27. Prediction of the partition coefficient of ethanol between the polar phase and the hydrocarbon (HC) phase for the ternary system of ethanol (1) – water (2) – heptane (3) at 293.15K using the 2B and 3B scheme for ethanol. The values of the interaction parameters are k_{12}= -0.11 (ECR), k_{13}=0.006 and k_{23}=0.0095 with 2B, or k_1 =0.0 (ECR), k_{13}=-0.009 and k_{23}=0.0095 with 3B. Experimental data are from Sørensen and Arlt[91].

3.6. Sensitivity analysis for multicomponent systems

When predicting multicomponent multiphase equilibria based solely on binary interaction parameters, it might be the case that no experimental data are available for all the binary systems, or no experimental data might be available at the desired temperature and pressure. For this reason a study of the influence of the binary interaction parameters on the prediction of the important alcohol partition coefficient for multicomponent mixtures is conducted, and the ability of CPA to perform phase equilibria calculations at different conditions based on the same binary interaction parameters is tested. For the reasons explained previously, only the 2B association scheme is considered for alcohols.

VLE predictions for the ternary ethanol – water – propane system at three different temperatures are performed based solely on the same binary interaction parameters. The interaction parameter for water – propane is obtained from the correlative equation $k_{ij}=-0.026*(\text{carbon number}) + 0.1915$. The binary interaction parameters of ethanol – water and ethanol – propane systems are dominant for an adequate prediction of the VLE of the ternary system; as could be anticipated, satisfactory prediction of the ternary system can be achieved even when no interaction parameter is used for water – propane. This is demonstrated in figure 3.28, which presents predictions of water/propane relative volatility as a function of the propane mole fraction in the liquid phase. CPA correctly predicts that an ethanol – water mixture can be separated by propane, since the water relative volatility with respect to propane is greater than unity for high propane concentrations in the liquid phase. In all cases the error in the vapor phase mole fraction is less than 1.5% while the percentage error in vapor pressure is less than 7 %.

LLE predictions of the methanol – water – n-butane and methanol – water – propane at two different temperatures are performed. The predictive performance of the model when using no binary interaction parameter for water – butane system is presented in figure 3.24 (case 3). For the system methanol – water – butane the amount of water in the hydrocarbon phase is very low, thus the correct representation of the n-butane – methanol system is crucial. The concentration of both water and butane are rarely high in the polar phase, thus the accurate representation of the water – alkane system is not very important for this type of calculations. On the other hand, a successful correlation of water – methanol and methanol – n-butane systems is required for a satisfactory prediction of the ternary system. Similar results are obtained for the other systems tested previously (i.e. methanol – water – hexane, ethanol – water – hexane and ethanol – water – heptane).

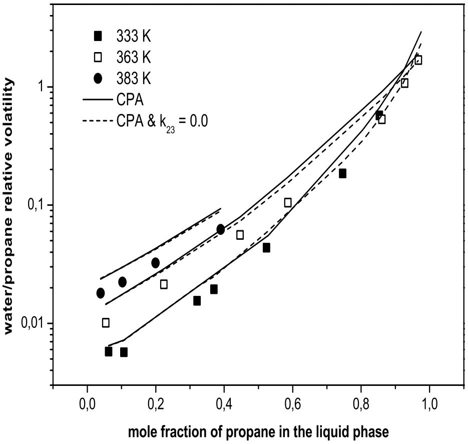


Figure 3.28. Prediction of the water/propane relative volatility for the ternary mixture ethanol (1) – water (2) – propane (3). The values of the interaction parameters are k_{12}= -0.11 (ECR), k_{13}=0.038 and k_{23}=0.1135 (solid line), or k_{23}=0.0 (dash line). Experimental data are taken from Horizoe[83].

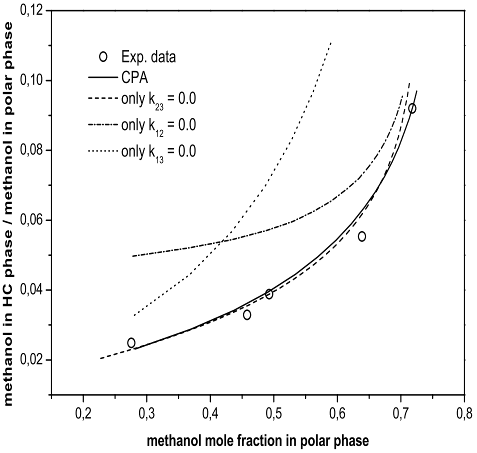


Figure 3.29. Prediction of the partition coefficient of methanol between the hydrocarbon (HC) and the polar phase for the ternary system of methanol (1) – water (2) – propane (3) at 293.15K. The values of the interaction parameters, when not set to zero, are k_{12}=-0.09 (ECR), k_{13}=0.026 and k_{23}= 0.1135. Experimental data are taken from Noda[81].

When the components which are in significant concentration in each phase are not well described, i.e. the methanol – propane system for the hydrocarbon phase and the binary system of methanol – water for the aqueous phase in the case of methanol – water – propane system, then very poor prediction of methanol distribution coefficient is obtained, as figure 3.29 demonstrates.

Finally, CPA has been also tested for the multicomponent system water – methanol – methane – propane – n-heptane for which extensive VLLE data is available[84] at different conditions (284.14 and 310.93K and pressures of 69, 138 and 206.8 bar). No interaction parameters are used for the hydrocarbon binary systems, since the SRK term of CPA provides satisfactory predictions of the phase behavior of size – symmetric alkane systems. The binary interaction parameter for methanol – methane system is k_{12}=0.0134 in accordance to previous study[4], while for water – hydrocarbon systems the binary interaction parameters are obtained from the correlative equation $k_{ij}=-0.026*(carbon\ number) + 0.1915$. The predictions of CPA are satisfactory at all temperatures and pressures studied. Similar results are obtained when the interaction parameters for the water – alkane systems are set equal to zero. This is elucidated by figure 3.30, which presents predictions of the methanol mole fraction in the three phases at 284.14K.

In conclusion, the CPA EoS predicts satisfactorily the multiphase equilibria of multicomponent water – alcohol – aliphatic hydrocarbon systems at various temperatures, based solely on the same binary interaction parameters, using the 2B scheme. As could be expected, the results indicate that the use of a binary interaction parameter for water – aliphatic hydrocarbon systems is not required for an adequate prediction of the industrially important partition coefficient of alcohol in the different phases.

3.7. Conclusions

In this chapter the implementation of the 3B association scheme for water and alcohols was investigated. It was concluded that for water the previously established 4C scheme provides systematically superior LLE and VLLE correlations of water – alkane systems.

In the case of n-alcohols the results with 2B and 3B schemes are summarized in table 3.10, showing which association scheme is best depending on the specific case. A plus (+) indicates that the results are satisfactory while a minus (-) indicates a problematic behavior. For VLE and SLE correlations of alcohol – hydrocarbons both schemes perform overall similar; however, 2B performs better in the alcohol diluted region. When methanol is assumed a 2-site molecule (2B), the LLE correlation of methanol – pentane, methanol – nonane and methanol – decane are superior with the 2B, but for all the other systems tested, both at low and high pressures the two schemes provide similar results. Similar is also the SLE predictive and correlative performance of the two schemes. However, both schemes provide poor VLE and LLE predictions (i.e. k_{12}=0.0). For VLE calculations, this is because of the high errors when the 2B scheme is used and the incorrect phase split in the case of the 3B. LLE calculations are very sensitive to the binary interaction parameter used (k_{12}), hence the use of zero binary interaction parameter (k_{12}=0) provides very poor results.

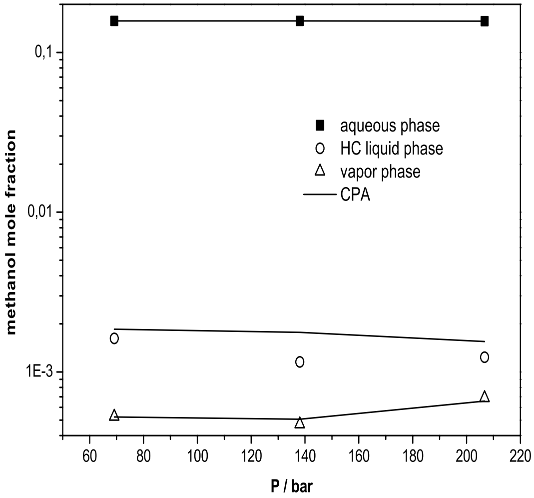


Figure 3.30. VLLE predictions for the system of methanol (1) – water (2) – methane (3) – propane (4) – n-heptane (5) at 284.14K. The values of the interaction parameters are k_{12}= -0.09 (ECR), k_{13}= 0.0134, k_{14}=0.026 and k_{15}=0.005. All binary interaction parameters for hydrocarbon – hydrocarbon systems are set equal to zero. Experimental data are taken from Cheng and Ng[84].

For cross – associating water – n-alcohol systems, both schemes provide very similar VLE correlation results with ECR, but only the assumption of a 2-site molecule for heavy alcohols provides adequate LLE calculations. An advantage gained with the 3B scheme for alcohols is the significantly lower k_{12} values required compared to the 2B, which consequently provides superior VLE predictions with the 2B scheme. However, the prediction of methanol distribution coefficient for ternary systems is among the cases where the 3B scheme fails. Especially due to the superior performance of the 3B scheme for multicomponent multiphase equilibria, the 2B scheme will be further used for alcohols.

Very satisfactory VLE and LLE predictions of multicomponent water – alcohol – hydrocarbon systems at various temperatures are obtained based solely on single binary interaction parameters, suggesting that the CPA EoS is a reliable model for multicomponent multiphase predictions at various conditions. Finally, a satisfactory description of the binary water – alcohol and alcohol – alkane systems is found to be crucial for an adequate prediction of the multicomponent systems.

Table 3.10. Evaluation of the performance of 2B and 3B scheme for alcohols. The symbol (+) indicates that the results are satisfactory while a minus (-) indicates a problematic behavior

Case	2B	3B
VLE correlation of n-alcohol – hydrocarbons	+	+
LLE correlation of n-alcohol – hydrocarbons	+	-
SLE correlation of n-alcohol – hydrocarbons	+	+
VLE prediction of n-alcohol – hydrocarbons	-	-
LLE prediction of n-alcohol – hydrocarbons	-	-
SLE prediction of n-alcohol – hydrocarbons	+	+
VLE correlation of water – n-alcohols	+	+
LLE correlation of water – n-alcohols	+	-
SLE correlation of methanol – water	+	+
VLE prediction of water – n-alcohols	-	+
LLE prediction of water – n-alcohols	-	-
SLE prediction of methanol – water	-	+
Prediction of methanol distribution coefficient for ternary systems	+	-
Prediction of ethanol distribution coefficient for ternary systems	+	+

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Chapter 4.

Application of the Cubic-Plus-Association (CPA) Equation of State to Mixtures with Aromatic Hydrocarbons

4.1. Introduction

The Cubic-Plus-Association (CPA) equation of state is applied to phase equilibria of mixtures containing alcohols, water and aromatic or olefinic hydrocarbons. Aromatic and olefinic hydrocarbons are also present in natural gas, together with aliphatics but in lower concentrations. Hence the solubility of BTEX compounds (benzene, toluene, ethylbenzene, xylenes) in aqueous systems of alcohols/glycols is of great importance both for economic and environmental reasons. For example, methanol and glycols, especially MEG, are used as gas-hydrate inhibitors in the production/processing of natural gas. Calculating the amount of the inhibitor needed requires use of an accurate model for phase equilibria of gas-oil-water-inhibitor mixtures and if the partitioning calculation is in error, the overall injection rate will also be in error[1,2].

Traditional thermodynamic models like cubic Equations of State (often even with advanced mixing rules) exhibit problems for multicomponent VLLE of water-alcohol/glycol-hydrocarbons[3], while it has been established that cubic EoS cannot be used for simultaneous VLE and LLE e.g. of alcohol-hydrocarbons with the same interaction parameters[4]. Relatively few investigations have been reported for multicomponent LLE of this type of mixtures[5-7].

Previously, CPA has been successfully applied to mixtures containing various associating compounds (alcohols, glycols, water) and aliphatic hydrocarbons. This chapter investigates the extension of the model to complex vapor-liquid-liquid equilibria with aromatic or olefinic hydrocarbons and polar chemical (water, alcohols). In parallel the importance of accounting for the solvation between aromatics/olefinics and a polar compound is evaluated, both for binary as well as for multicomponent systems. In all of the applications presented in this chapter, alcohols have been treated as two-site molecules (2B), while water has been treated as four-site molecules (4C) in accordance to the results of chapter 3.

4.2. Extension of the CPA EoS to Aromatic and Olefinic Hydrocarbons

Although the CPA EoS is already presented in detail in chapter 1, this section discuss briefly the extension of the model to mixtures of polar chemicals and aromatic or olefinic hydrocarbons. Since aromatic (or olefinic) hydrocarbons do not self–associate, only the three parameters for the physical term of the model are being optimized for CPA. In this manner however no cross – association is allowed, given that both the cross – association energy and volume parameters are zero, and therefore the use of either CR-1 (equation 1.13) or ECR (equation 1.14) results in zero association strength. However, mixtures containing aromatic or olefinic hydrocarbons and polar compounds e.g. water or alcohols are characterized by the solvation that is known to exist between these compounds[8-10], due to the π electrons in the aromatic ring which make the aromatics electronegative enough to be bonded with hydrogen. The increased solubility of aromatic hydrocarbons in water, compared to the aliphatic ones with the same carbon number is a typical evidence of the solvation. For example, the solubility of benzene in water is two orders of magnitude higher that the solubility of the "homomorph" hexane (i.e. alkane with the same carbon number).

To account for solvation, the modified CR-1 (mCR-1) combining rule is used, as already discussed in chapter 1, allowing, however, the cross-association volume $\beta^{A_iB_j}$ (or BETCR) to be optimized from experimental data. Thus, the cross-association energy parameter for associating-aromatic or olefinic mixtures is equal to the value of the associating compound (water, alcohol or glycol) divided by two:

$$\varepsilon^{A_iB_j} = \frac{\varepsilon_{associating}}{2} \text{ and } \beta^{A_iB_j} = BETCR \text{ (fitted)} \tag{4.1}$$

An alternative approach investigated in this chapter is the use of a modified ECR combining rule, where the cross-association strength $\Delta^{A_iB_j}$ which is normally calculated from equation (1.3), is directly fitted to a constant value. The difference in the two approaches is that in the first case, the in-built temperature dependency of the association strength (see equation 1.3) for solvating systems is retained. The two approaches will be further discussed in section 4.3, which presents VLLE of binary water – aromatic hydrocarbons systems over extended temperature ranges.

4.3. Correlation of VLLE of water with aromatic and olefinic hydrocarbons

It has been previously showed that CPA can correlate satisfactorily water-alkane VLLE using a single interaction parameter[11,12]. Both the water solubility in the hydrocarbon phase and the very low alkane solubility in water phase are adequately represented, except for the minimum in the alkane solubility at low temperatures which may be associated to the hydrophobic effect[13]. Voutsas et al.[12] showed that CPA correlates the alkene solubility in the aqueous phase systematically inferior compared to the solubility of the homomorph alkane, when no solvation between water and the olefinic hydrocarbons is allowed. However CPA performs better than several SAFT-variants for water-alkane LLE [12,14].

Using data from water-propane up to water-decane, a generalized expression for the interaction parameter can be obtained using the equation:

$$k_{12} = -\,0.026 * (N_c) + 0.1915 \tag{4.2}$$

where N_c is the carbon number of the alkane. Table 4.1 presents the percentage average absolute deviation (% AAD) in the solubility of water in the hydrocarbon and the vapor phase as well as in the solubility of hydrocarbon in the aqueous phase for five water-alkane systems.

Table 4.1. Percentage Average Absolute Deviation (% AAD) between experimental and calculated water solubilities in the hydrocarbon phase (X_{water}) or the vapor phase (y_{water}) and hydrocarbon solubilities in the aqueous phase (X_{HC}) using the generalized expression for the interaction parameter, equation (4.2).

Hydrocarbon	T range [K]	k_{12}	% AAD in X_{water}	% AAD in X_{HC}	% AAD in y_{water}
propane	278 – 366	0.1135	3.4	35.9	4.1
butane	310 – 420	0.0875	11.7	26.5	9.5
n-pentane	280 – 420	0.0615	13.4	28.4	-
n-hexane	280 – 473	0.0355	11.9	31.1	-
n-heptane	280 – 420	0.0095	11.5	63.3	-
n-octane	310 - 550	-0.0165	9.7	44.1	1.9
n-decane	290 – 566	-0.0685	8.2	264	-

As table 4.1 presents, the water solubility in the hydrocarbon phase and the gas phase water content are quite satisfactorily correlated using equation (4.2). The overall correlation of the hydrocarbon solubility in the aqueous phase is slightly inferior (but still adequate compared to various SAFT-variants), mainly due to the minimum in solubility at low temperatures which cannot be described using CPA. However the performance of the model at elevated temperatures is satisfactory especially compared to the lower temperatures (i.e. where the minimum in solubility occurs). Slightly better results are obtained when the optimum interaction parameter (k_{12}) per system is used. An exception seems to be the correlation of the n-decane solubility in water, in the case of which CPA overestimates the solubility of n-decane in water. Even when the binary interaction parameter is explicitly fitted to experimental LLE data (thus not using the generalized expression of equation 4.2) the results are only slightly improved. This behavior can be attributed to the fact that CPA cannot represent the temperature dependency of the solubility of n-decane in water. It must be mentioned that, as Economou et al.[22] also discuss, there is a remarkable disagreement regarding the solubility of n-decane in water among the various experimental sources. For example, the experimental data from Guerrant et al.[15] for the same system (read from the graph of the article by Economou et al.[22]) are in much better agreement with CPA calculations, as figure 4.1 demonstrates. However, for the evaluation of the model in table 4.1 only experimental data from Economou et al.[22] are used, since they cover an extended temperature range. Interestingly enough Tsonopoulos omits in a recent publication[49] a generalized expression for the mutual solubility of n-decane in water, even if experimental data were available over an extended temperature and pressure range[22].

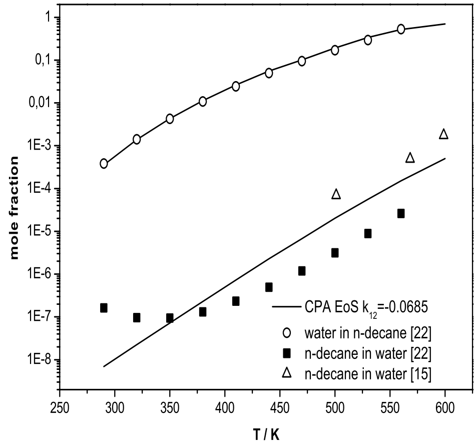

Figure 4.1. LLE correlation of water - decane with a binary interaction parameter obtained from equation (4.2) Experimental data are taken from Guerrant et al.[15] and Economou et al.[22].

When dealing with water – aromatic hydrocarbon mixtures a first issue that should be considered is the importance of the solvation. As already mentioned, the solubility of the aromatic hydrocarbons in water is two orders of magnitude higher than the aliphatic ones with the same carbon number; this is a clear physical indication for the importance of solvation for such systems. It is concluded that only when accounting for the solvation, both solubilities can adequately be correlated with the CPA EoS. A simplified approach with the use of only a binary interaction parameter (k_{12}) significantly fails to correlate the hydrocarbon solubility when fitting the k_{12} to the water one and vice versa.

As discussed in section 4.2, two different ways for accounting for the solvation might be considered, either using mCR-1 (i.e. equation (4.1)) and optimizing the *BETCR*, or optimizing the association strength $\Delta^{A_iB_j}$. Two parameters have to be fitted for CPA to experimental data, i.e. including the k_{12} for the physical term. The importance of retaining the in-built temperature dependency of the first approach (i.e. modified CR-1) is demonstrated in figure 4.2. When the association strength is optimized to a fixed and temperature independent value (dashed line) less satisfactory results are obtained, thus emphasizing the importance of the solvating scheme with the in-built temperature dependency discussed previously (equation 4.1).

The possibility of reducing the adjustable parameters is also investigated. It is concluded that for water/aromatics a single binary interaction parameter which accounts for the solvation can be fitted to experimental LLE data. The interaction parameter of the physical term of the model (k_{12}) can be obtained from the corresponding "homomorph" alkane e.g. the k_{12} of water/benzene is assumed to be that of water/hexane etc. Very similar results can be obtained when optimizing both k_{12} and BETCR (or both k_{12} and $\Delta^{A_iB_j}$ with the modified ECR). Table 4.2 summarizes the results for all water-aromatic systems considered.

Solvation is important for water-alkenes as well. The solubility of 1-alkenes in water is one order of magnitude higher than the solubility of the corresponding aliphatic hydrocarbon with the same carbon number. This is due to the double bond between the first and the second carbon in the carbon chain, which results in an increased electronegativity of 1-alkenes; hence it can act as electron donor, similar to the case of the aromatics. The LLE of water – 1-alkene binary systems was studied by Voutsas et al.[12] and the overall results suggest that CPA, without accounting for solvation effects, can very satisfactorily correlate the solubility of water in 1-alkene, but fails in the other end (by an order of magnitude or more).

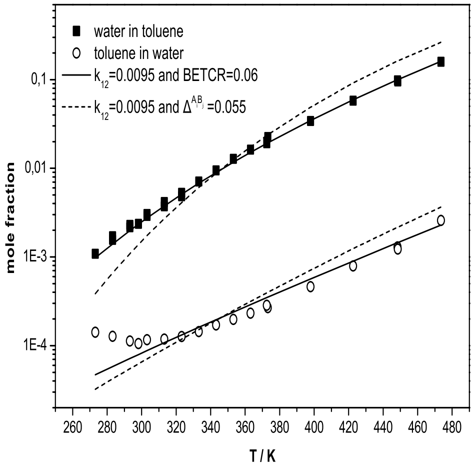

Figure 4.2. LLE correlation of the system toluene – water using two different approaches: homomorph approach for k_{12} and optimizing BETCR (mCR-1 solid line), and homomorph approach for k_{12} and optimizing a constant temperature-independent value of association strength $\Delta^{A_iB_j}$ (dashed line). Experimental data are taken from references 16-18.

In this work the LLE correlation of three systems, namely water – 1-hexene, water – 1-octene and water – 1-decene is presented. All 1-alkenes are treated as inert but cross – associating with water (as given by equation 4.1). Figures 4.4 and 4.5 show some typical results. Satisfactory results are obtained and moreover the same BETCR parameter can be used, suggesting that the contribution of the double bond is the same when the physical interactions are adequately optimized using the homomorph k_{12} i.e. from the corresponding water/alkane system, similarly to water-aromatic hydrocarbons. All results are summarized in Table 4.2.

An exception is the system water – 1-decene, where CPA overestimates the solubility of 1-decene in water, as presented in figure 4.5. This behavior cannot be attributed to the homomorph approach (used for obtaining the binary interaction parameter k_{12}) or the BETCR parameter used (equal to that for 1-hexene and 1-octene). Even when both parameters are explicitly fitted to experimental data, (with optimized parameters k_{12}=0.03 and BETCR=0.032) the model still overestimates significantly the calculated solubility of 1-decene in water. Hence, as also experienced for water – decane, this behavior might be attributed to the fact that CPA cannot represent adequately the temperature dependency of the 1-decene solubility in water. Tsonopoulos[48] however states in a recent publication that the mutual solubilities of 1-decene in water are clearly suspect.

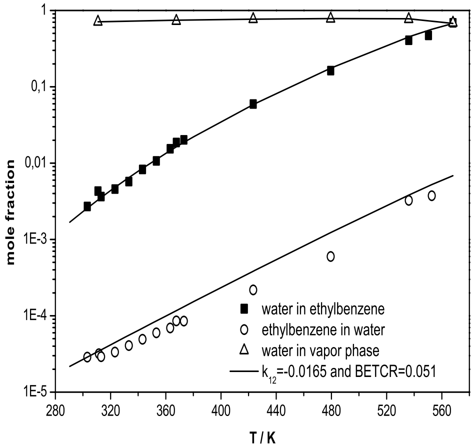

Figure 4.3. VLLE of water – ethylbenzene system with the CPA EoS. Experimental data are taken from Chen and Wagner[19], Heidman et al.[20], Owens et al.[21]

Table 4.2. Percentage Average Absolute Deviation (% AAD) between experimental and calculated water solubilities in the hydrocarbon phase (X_{water}) or the vapor phase (y_{water}) and hydrocarbon solubilities in the aqueous phase (X_{HC}) using the generalized expression for the interaction parameter, equation (4.2).

Hydrocarbon	**T range [K]**	**k_{12}**	**BETCR**	**% AAD in X_{water}**	**% AAD in X_{HC}**	**% AAD in y_{water}**
benzene	273 - 473	0.0355	0.079	5.3	19.5	-
toluene	273 – 473	0.0095	0.06	5.1	23.5	-
ethylbenzene	303 - 568	-0.0165	0.051	6.5	47.1	1.1
propylbenzene	280 – 420	-0.0425	0.041	14.3	38.5	-
m-xylene	373 - 473	-0.0165	0.039	3.7	8.3	-
1-hexene	310 - 496	0.0355	0.021	7.6	29.3	1.2
1-octene	310 - 540	-0.0165	0.021	4.7	23.4	1.1
1-decene	310 - 550	-0.0685	0.021	12.7	288	-

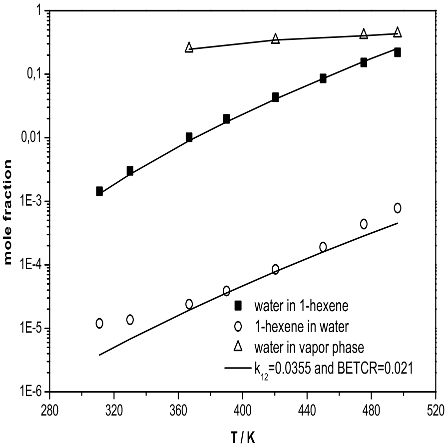

Figure 4.4. VLLE of water – 1-hexene system with the CPA EoS. Experimental data are taken from Economou et al.[22]

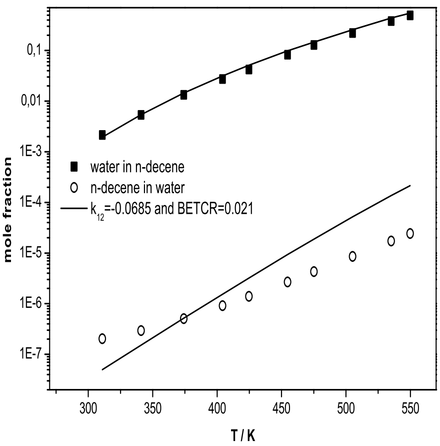

Figure 4.5. VLLE of water – 1-decene system with the CPA EoS. Experimental data are taken from Economou et al.[22]

4.4. VLE for alcohol-aromatic hydrocarbons

Extensive VLE data are available for methanol and ethanol with aromatic hydrocarbons (benzene, toluene) at various temperatures. No LLE data were found and it seems that these alcohols are miscible with aromatic hydrocarbons down to very low temperatures. This is not the case for mixtures with aliphatic hydrocarbons e.g. methanol with either hexane or heptane exhibit LLE below 310/325 K as shown in chapter 3. This phenomenon alone indicates that some solvation must be present between alcohols and aromatic hydrocarbons.

As in the case of water – aromatics, the first issue to be investigated is to what extent CPA should explicitly account for solvation, or if this can be taken into account via the physical term of the model with the use of an appropriate binary interaction parameter (k_{12}). Systematic investigations in this chapter demonstrate that accounting for solvation in CPA results in only slight improvement in the VLE of alcohol-aromatic hydrocarbons compared to the results without solvation, as table 4.3 demonstrates. Equally good results are obtained either when benzene is assumed completely inert (no solvation) or when allowed to solvate with methanol, as can be seen by a typical result in figure

4.6. For example, the methanol/benzene system was studied over an extensive temperature range (298-493K) and CPA even with k_{12}=0 and no solvation results in an average error in pressure of only 2.5%. Studies with other SAFT-type approaches led to the same conclusion: very good results for alcohol-aromatics can be obtained even if solvation is not explicitly accounted for [23-26].

The same good VLE performance and similarities in the results are obtained for all systems studied over the temperature range that data were available. The importance of the solvation is expected to be pronounced at low temperatures, where however some uncertainties in experimental measurements are detected and thus those data were excluded for the study. More specifically VLE data for methanol – benzene system are measured by Schmidt[50] over a temperature range of 273 – 373K. A comparison of those measurements to other experimental sources at higher temperatures indicates that Schmidt's measurements at low methanol concentration are erroneous. All other sources are consistent with each other; hence the data of Schmidt[50] are rejected from the study. No other data at lower temperatures than those presented in table 4.3 are available to the best of our knowledge.

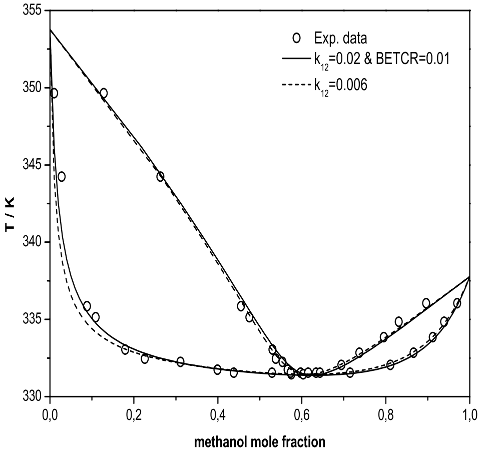

Figure 4.6. VLE diagram of methanol – benzene at 1 bar, using two different cases: Case 1 with the dashed line is when benzene is assumed to be completely inert (only k_{12} fitted) while case 2 with the solid line is when benzene is allowed to solvate with methanol (k_{12} and BETCR fitted). Experimental data are taken from Nagata[27].

Solvation is somewhat more important in the methanol systems, but almost of no significance for ethanol in mixtures with BTEX compounds. The importance of the solvation is more evident at dilute solutions e.g. infinite dilution activity coefficients (or limiting activity coefficients) especially of methanol in hydrocarbons. Typical results shown in figures 4.7 and 4.9 demonstrate that indeed in these cases use of CPA with case 2 (accounting for the solvation) yields better results than when aromatics are assumed to be completely inert (case 1). On the other hand, in the case of ethanol, both cases perform similarly as figures 4.8 and 4.10 indicate. It seems that in the case of ethanol the use of a higher value of binary interaction parameter (compared to methanol) adequately accounts for the solvating phenomena. The importance of solvation even for methanol can be, however, still debated as such situations of low temperatures and infinite dilution studies represent extreme cases. The two schemes for alcohol-aromatic systems (with and without solvation) will be further tested in the next section for multicomponent systems.

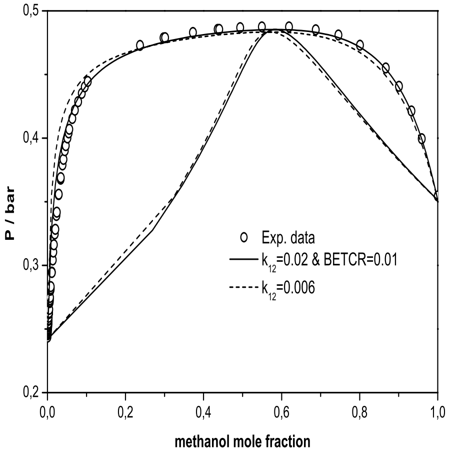

Figure 4.7. P-x diagram of methanol – benzene at 313.15K, using the two different cases (as in figure 4.5). Experimental data are taken from Oracz and Kolasinska[28]

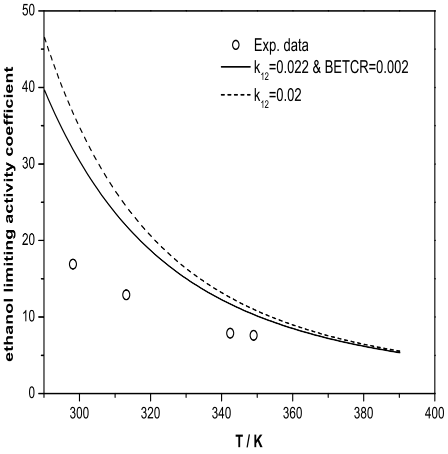

Figure 4.8. Limiting activity coefficients of ethanol in benzene using the two different cases (as in figure 4.5). Experimental data are taken from Landau et al.[29]

4.5. Prediction of LLE for water-alcohol-aromatic hydrocarbons

Three ternary water-alcohol-aromatic hydrocarbon systems for which there are extensive LLE data have been tested with CPA. Finally, the quaternary VLLE water-methanol-methane-toluene system has been considered as well. Two cases have been considered, case 1 (no solvation for the alcohol-hydrocarbon binary) and case 2 (solvation is accounted for between alcohol-hydrocarbon). The interaction parameters for water-alcohol systems are according to chapter 2, k_{12}=-0.09 for methanol – water and k_{12}=-0.11 for ethanol water system, respectively, using ECR. Water-aromatic hydrocarbons are always considered as solvating systems using the homomorph approach for the k_{12}, with the parameters presented in section 4.2. Very good results are obtained as shown for some typical systems in figures 4.11-4.16. Results are equally good (often better) for the binodal curves, thus only partition coefficients are presented, since they represent a more sensitive indicator and they are often more important in practical applications.

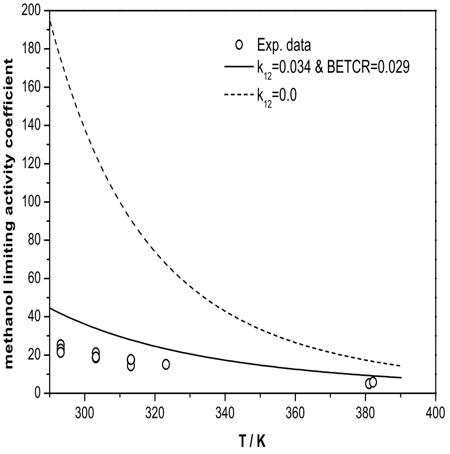

Figure 4.9. Limiting activity coefficients of methanol in toluene using the two different cases (as in figure 4.5). Experimental data are taken from Vrbka et al.[30]

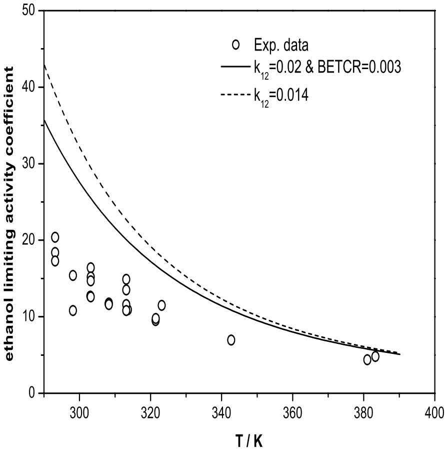

Figure 4.10. Limiting activity coefficients of ethanol in toluene using the two different cases (as in figure 4.5). Experimental data are taken from Vrbka et al.[30]

Table 4.3. VLE correlation results for alcohol – aromatic hydrocarbons at different temperatures. Two cases are considered: Case 1 assumes that the aromatic hydrocarbon is completely inert (i.e. no solvation) while case 2 allows the aromatic hydrocarbon to cross – associate with the alcohol.

			Case 1			**Case 2**			
System	**Ref**	**T / K**	***k*$_{12}$**	**ΔP %**	**Δy %**	***k*$_{12}$**	**BETCR**	**ΔP %**	**Δy %**
Methanol – benzene	31, 32	298.15	0.006	0.5	0.6	0.02	0.01	0.8	0.9
	33	308.15	0.006	4.4	2.8	0.02	0.01	2.5	2.1
	34	318.15	0.006	4	2.7	0.02	0.01	2.1	1.7
	33	328.15	0.006	3.5	2	0.02	0.01	2.0	1.6
	35	373.15	0.006	1.9	1	0.02	0.01	1.3	0.9
	35	393.15	0.006	1.5	0.9	0.02	0.01	1.2	0.9
	35	413.15	0.006	2.2	1.3	0.02	0.01	1.6	1.0
	35	433.15	0.006	1.9	1.1	0.02	0.01	1.2	0.7
	35	453.15	0.006	1.9	1.1	0.02	0.01	1.6	0.6
	35	473.15	0.006	1.9	0.6	0.02	0.01	1.5	0.5
	35	493.15	0.006	1.3	1.2	0.02	0.01	1.0	1.2
Methanol – toluene	36	318.15	0.0	4.3	1.4	0.034	0.029	0.9	0.7
Ethanol – benzene	32	298.15	0.02	1.4	1	0.022	0.002	1.1	0.9
	37	318.15	0.02	0.9	0.5	0.022	0.002	1.0	0.5
	38	328.22	0.02	1.7	0.6	0.022	0.002	1.9	0.7
Ethanol – toluene	39	308.15	0.014	0.8	0.4	0.02	0.003	0.7	0.3
	40	318.15	0.014	2.0	1.4	0.02	0.003	1.4	1.0
	39	328.15	0.014	1.0	0.5	0.02	0.003	0.8	0.4
	41	338.15	0.014	2.0	1.1	0.02	0.003	1.6	1.0
	41	348.15	0.014	2.2	1.0	0.02	0.003	1.7	1.0
Average				**2.0**	**1.2**			**1.4**	**0.9**

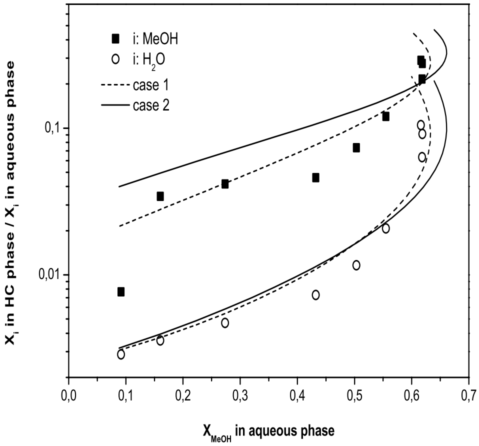

Figure 4.11. Prediction of methanol and water partition coefficient for the ternary system water(1) – methanol(2) – benzene(3) at 293.15K, using the two cases. Case 1: k_{23}=0.006 while Case 2: k_{23}=0.02 & BETCR=0.01. Experimental data are taken from Triday[42].

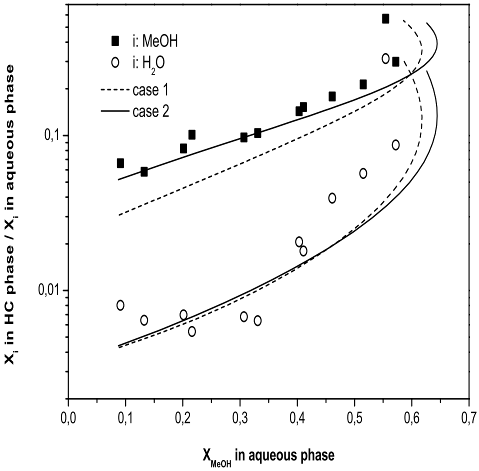

Figure 4.12. Prediction of methanol and water partition coefficient for the ternary system water(1) – methanol(2) – benzene(3) at 303.15K, using the two cases (as in figure 4.11). The binary parameters used are the same as at 293.15K. Experimental data are taken from Gramajo de Doz et al.[43].

The results with cases 1 and 2 are in most cases similar, indicating that accounting for the solvation between alcohol and aromatic hydrocarbons is often not very important for obtaining satisfactory multicomponent LLE predictions with CPA. It seems though that solvation yields improved results for the quaternary mixture considered. The interaction parameters for the binaries involved in the multicomponent system are presented in Table 4.5.

Another interesting issue, is the U-type shape that some experimental data reveal for water-methanol-benzene, e.g. as shown in figure 4.13. Even though most data exhibit an increasing trend of the partition coefficients with the concentration of the alcohol in the aqueous phase e.g. figures 4.11, 4.12, 4.14 and 4.15, some measurements at infinite alcohol concentration indicate a sudden increase in the partition coefficient of the alcohol. According to Reid and Prausnitz[47] knowledge of the infinite dilution of methanol in the two phases provides a good approximation of the experimental distribution coefficient at infinite conditions. Hence the methanol distribution coefficient can be approximated by the following equation:

$$K^{\infty}_{methanol} = \frac{\gamma^{\infty}_{methanol\ in\ hydrocarbon}}{\gamma^{\infty}_{methanol\ in\ water}} \tag{4.3}$$

We further evaluated the $K^{\infty}_{methanol}$ values calculated by equation (4.3) using CPA and accounting for the solvation with mCR-1, because this was shown to provide more accurate infinite dilution activity coefficient calculations. Those values were further compared to the experimental ones, also in cases where more than one experimental source was available. The following summarize our observations:

i) For the ternary system water – methanol – benzene the experimental partition coefficient of methanol at 303.15K is 0.066 (Gramajo de Doz et al.[43]) or 0.438 (DECHEMA, Sørensen and Arlt[44]). The partition coefficient of methanol in the latter case shows a U-type shape, which is not the case for the data from Gramajo de Doz[43]. The calculated value with the CPA is of the order of 0.09; hence, for the evaluation of the model in figure 4.12 the experimental data from Gramajo de Doz et al.[43] is used. However, at elevated temperatures the only available experimental data[44] show a U-type shape.

ii) For methanol – water –toluene system experimental values of partition coefficient are within the range of 0.014[44]-0.11[45] at 298.15K while the CPA calculations are 0.08. The experimental partition coefficient of methanol for both sources does not show the U-type shape, as was the case before.

No U-shape type of ethanol partition coefficient is evident for the ternary system water – ethanol – benzene. Hence infinite dilution partition coefficients around 0.5 (figure 4.13) might be questionable.

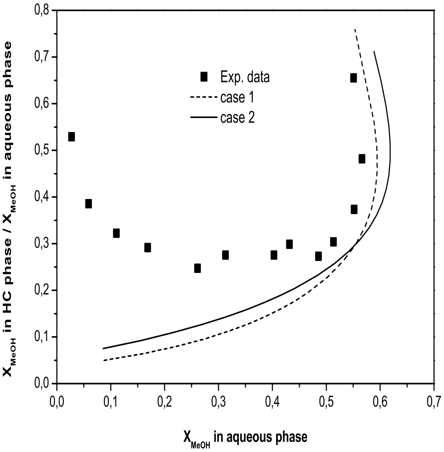

Figure 4.13. Prediction of methanol partition coefficient for the ternary system water(1) – methanol(2) – benzene(3) at 318.15K, using the two cases. The binary parameters used are the same as at 293.15K. Experimental data are taken from Sørensen and Arlt[44].

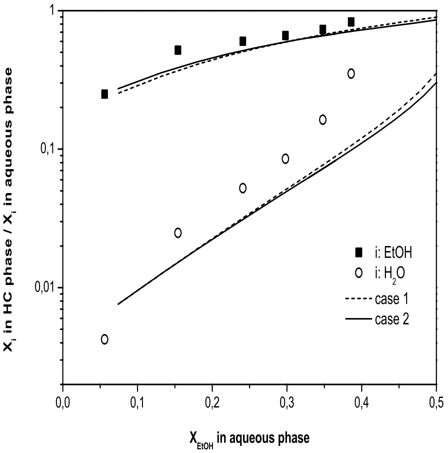

Figure 4.14. Prediction of ethanol & water partition coefficient for the ternary system water(1) – ethanol(2) – benzene(3) at 308.15K. Case 1: k_{23}=0.02 while Case 2: k_{23}=0.022 and BETCR=0.002. The ECR is used for ethanol/water with k_{12}=-0.11. Experimental data are from Sørensen and Arlt[44].

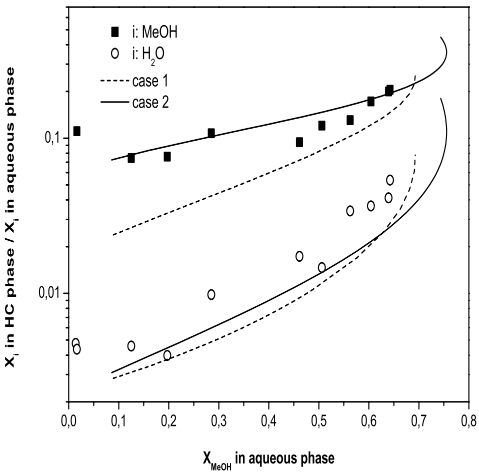

Figure 4.15. Prediction of methanol & water partition coefficient for the ternary system water(1) – methanol(2) – toluene(3) at 298.15K. Case 1: k_{23}=0.0 while Case 2: k_{23}=0.034 and BETCR=0.029. Experimental data are taken from Tamura et al.[45]

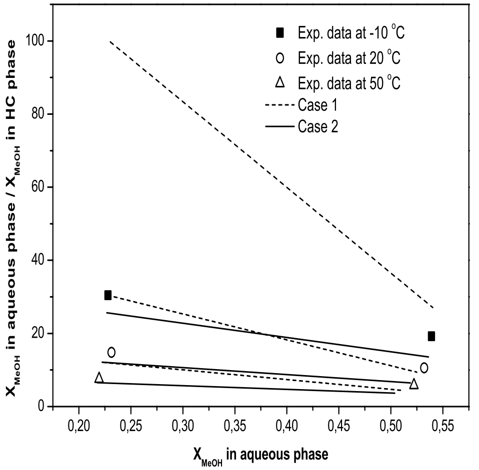

Figure 4.16. Prediction of methanol partition coefficients for the quaternary system water – methanol – toluene – methane. Parameters are obtained from table 4.6. Experimental data are taken from Chen et.al.[46].

Table 4.4. VLLE prediction results for the quaternary system water(1) – methanol(2) – methane(3) – toluene(4) with the CPA EoS, expressed as %AAD of the mole fraction (x) of the compound i in each phase. The two different cases are as explained in section 4.5.

				Case 1			Case 2		
T / K	P / bar	component	FEED	Vapor Phase	HC Liquid Phase	Aqueous Liquid Phase	Vapor Phase	HC Liquid Phase	Aqueous Liquid Phase
263.15	80.2	H_2O	0.3388	79.2	23.7	0.4	79.0	2.1	0.1
		MeOH	0.1027	20.6	69.2	0.9	19.7	18.2	0.5
		CH_4	0.3351	0.1	8.8	10.8	0.1	7.4	7.8
		C_7H_8	0.2234	1.0	1.7	0.6	3.8	2.2	26.8
263.15	80.05	H_2O	0.1575	89.2	26.8	1.0	89.2	4.4	1.6
		MeOH	0.207	0.4	28.6	0.3	1.1	40.8	0.5
		CH_4	0.3813	0.1	7.4	24.1	0.1	5.7	14.4
		C_7H_8	0.2542	1.1	1.0	10.2	2.6	3.1	48.7
293.15	94.2	H_2O	0.3441	13.6	4.2	13.6	14.9	17.2	1.0
		MeOH	0.1044	18.3	52.1	18.3	17.0	17.2	3.9
		CH_4	0.3309	0.1	2.4	0.1	0.1	4.0	30.9
		C_7H_8	0.2206	31.5	1.8	31.5	28.3	0.8	19.1
293.15	96.1	H_2O	0.1644	45.7	1.4	45.7	45.4	11.3	3.2
		MeOH	0.2159	10.2	11.2	10.2	12.1	59.2	2.5
		CH_4	0.3718	0.1	1.3	0.1	0.1	3.2	19.9
		C_7H_8	0.2479	3.5	0.4	3.5	0.4	3.2	31.2
323.15	80.3	H_2O	0.3823	18.3	7.2	0.8	17.2	4.4	0.1
		MeOH	0.1159	4.9	36.3	1.8	5.8	15.2	0.9
		CH_4	0.3011	0.1	5.1	49.3	0.1	6.9	43.0
		C_7H_8	0.2007	7.8	2.6	40.7	5.9	1.0	9.7
323.15	80.9	H_2O	0.1796	10.7	11.7	1.3	10.1	8.6	4.8
		MeOH	0.2359	6.8	28.7	2.4	9.2	53.7	3.5
		CH_4	0.3507	0.1	7.3	19.9	0.1	9.0	8.0
		C_7H_8	0.2338	11.8	2.0	18.8	7.9	4.6	23.9

Table 4.5. CPA binary interaction parameters (mCR-1 always for toluene – water interactions) used for the prediction of the quaternary system.

	MeOH	**H_2O**	**C_7H_8**	**CH_4**
MeOH		-0.09 & ECR	Case 1: k_{12} =0.0 Case 2 (mCR-1): k_{12} =0.034 & BETCR=0.029	0.0134
H_2O			mCR-1: 0.0095 & BETCR=0.06	-0.045
C_7H_8				0.0

4.6. Conclusions

The Cubic-Plus-Association (CPA) equation of state has been applied in this work to phase equilibria of mixtures containing water, alcohols and aromatic or olefinic hydrocarbons. Emphasis was given on simultaneous VLE/LLE calculations, infinite dilution conditions and especially multicomponent multiphase equilibria, which are important in many practical applications. Aromatic and olefinic hydrocarbons are known to solvate with polar compounds like water and alcohols and a solvation scheme has been employed with CPA maintaining the temperature dependency of the association strength. Satisfactory results are obtained for LLE of water-aromatics/olefinics and for both the water and hydrocarbon solubilities. For water/aromatics, olefinics, only the “solvating” parameter is fitted to the data and the interaction parameter of the physical term is obtained from water/aliphatic hydrocarbons. Solvation phenomena are, compared to mixtures with water, less important for alcohol-aromatic hydrocarbons except at infinite dilution or very low temperatures. Finally, CPA predictions of LLE for multicomponent water-alcohol-aromatic hydrocarbons are satisfactory, taking into account also the uncertainties of the experimental data. All multicomponent calculations are based solely on binary interaction parameters estimated from binary data. The results of this work demonstrate that CPA is a flexible thermodynamic tool in modeling vapor-liquid and liquid-liquid equilibria of aqueous multicomponent mixtures containing alcohols and aliphatic, aromatic and olefinic hydrocarbons.

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Chapter 5.

Liquid – Liquid Equilibria for Binary and Ternary Systems Containing Glycols, Aromatic Hydrocarbons and Water. Experimental Measurements and Modeling.

5.1. Introduction

Aqueous mixtures of glycols with hydrocarbons, both aliphatics and aromatics, are of great interest to the oil and gas industry, mainly due to the use of glycols as hydrate inhibitors as well as for drying the gas in dehydration units. Besides the use of MEG as gas hydrate inhibitor, other glycols have also important applications where physico-chemical data are required, e.g. TEG is used in approximately 95% of the glycol dehydration units for natural gas streams (due to its chemical stability, low cost and high affinity to water). The solubility of aromatic hydrocarbons is also very important due to the hydrocarbon emissions from glycol regeneration units.

Although experimental data of glycols with aliphatic hydrocarbons were recently measured by Derawi et al.[1] (only binary systems), reliable experimental data of glycols with aromatic hydrocarbons, and especially in the presence of water, are very scarce. Extensive data can be found only for the binary mixtures of diethylene glycol (DEG) with benzene or toluene and the ternary mixture DEG - water – benzene[2], probably due to the fact that DEG was the standard dehydration solvent for many years and therefore more extensively studied. TEG, however, became more popular as the latter is more favorable with respect to loss and degradation. In this work, experimental LLE measurements of four binary glycol - aromatic hydrocarbon systems and three ternary systems containing water have been measured at atmospheric pressure. The measured systems are monoethylene glycol (MEG) - benzene or toluene, triethylene glycol (TEG) - benzene or toluene, MEG - water - benzene, MEG - water - toluene, and TEG - water - toluene.

From the thermodynamic point of view, accurate description of the phase equilibria of such systems is a challenging problem, usually requiring models which explicitly account for association between like molecules (i.e. two molecules of water) or solvation between unlike molecules, such as the interactions between glycols, water and aromatic hydrocarbons. In the previous chapter the CPA EoS was successfully applied to binary and ternary systems containing water, alcohols and aromatic hydrocarbons. A way to account for the interactions between water and the electronegative aromatic ring was presented through the use of mCR-1, retaining the in-built temperature dependency of the association strength. The experimental measurements presented in this work as well as existing data are correlated in the case of binary systems or predicted in the case of ternary systems with the CPA EoS in order to further validate the applicability of the model to systems containing aromatic hydrocarbons and glycols.

5.2. Experimental procedure

The chemicals used in this work are tabulated in Table 5.1. They were used without further purification.

Table 5.1. Specifications of the chemicals used in this work.

Chemical	Specified purity	Water content	Supplier
Ethylene glycol (MEG)	≥99.5 %	≤0.10 %	Merck
Triethylene glycol (TEG)	>99 %	≤0.30 %	Merck
Toluene	≥99.9 %	≤0.03 %	Merck
Benzene	≥99.7 %	≤0.03 %	Merck
Acetone	≥99.5 %	≤0.05 %	Merck

5.2.1. Mixing and equilibrium

Mixtures of known mass fraction of glycols, water and hydrocarbons were vigorously shaken for approximately 24 h in an air-heated oven. For binary systems, the mass fraction was approximately 0.5, while for the ternary systems a mass fraction of 0.5 of the hydrocarbon was added to a mixture of glycol and water; in the latter the mass fraction of glycol in the aqueous phase would vary from 40 % to 90 %, since this range of glycol composition is of interest for industrial applications in the North Sea. The temperature of the mixing was in principle the same as the temperature of the equilibrium measurements. However, for the measurements at low temperatures, a higher mixing temperature was chosen in order to achieve an adequate mixing of the components before equilibration.

The solutions, after mixing, were transferred in equilibrium cells to obtain phase equilibria at the desired temperature. The cells were made of glass, and sampling was possible from each phase, since the cells were equipped with several orifices sealed with Teflon-coated septa. The solutions were left at the desired temperature for 24 h in order to obtain equilibrium. When the mixture was transferred to the equilibrium cells for separation, both phases were cloudy while after 24 h the phases were completely transparent, indicating that the mixture reached the equilibrium state. Especially at low temperatures the equilibrium was further ensured, by sampling and analyzing the traces of the compounds in each phase within a time difference of 12h after the first analysis (typically taking place after 24 h as already mentioned); the equality of the analyzed traces is a further indication of equilibrium. The desired time to reach equilibrium for the mixtures at low temperatures (up to 10^{o}C) is approximately 2 days. A DOSTMANN P500 thermometer ($\pm$ 0.1 °C) was used for the temperature measurements.

5.2.2. Sampling and Analysis

Samples from the two phases were withdrawn manually with a preheated syringe and needle after equilibration in order to avoid phase separation during sampling. For the same reason, acetone was added to the sample before the analysis. After sampling and mixing with acetone, the amounts of the desired components were analyzed using gas chromatography (GC). The GC apparatus was calibrated based on external standards of mixtures of acetone with a known composition of the component that was going to be determined. Four samples of each standard mixture were analyzed and the average of the measurements was considered as the actual composition of the component. The use of several calibrating standards covering a limited concentration range, which is close to the concentration range of the actual experimental measurements (in order to increase the accuracy of the measurements) results in a reference curve. The reference curve relates the ratio between peak area of the chromatograph and the amount of injected matter and has to be linear for reliable measurements. The uncertainty of the measurements is estimated to be 2 % in the worst case (for the most diluted component for the ternary systems). The uncertainty of the water content in the polar phase is estimated to be less than 1 %.

The GC detectors would cause a drift of the signal of the GC over time; therefore the calibration curve is time – sensitive. In order to avoid such uncertainties, the actual samples were analyzed as close (in time) as possible after the calibration curve was generated. In order however to further ensure that such an effect does not occur when analyzing the actual samples, standards samples from the same solutions which were used for the calibration of the apparatus were analyzed first. When the mean value of the standard samples exceeded the uncertainty, new calibration curves were made. Two experiments were carried out in parallel in order to check the reproducibility of the data; for the binary systems the results were reproducible in all cases within the experimental uncertainty of the measured values, while for the ternary systems the reproducibility can be up to 3% in the worst case.

Three different GC apparatus, equipped with different columns and detectors were used to analyze the trace amounts of the components involved in this study. The characteristics of the chromatographs are tabulated in Table 5.2. More specifically, GC-2 was used to obtain the amount of glycol in the hydrocarbon phase. GC-3 was used to analyze the trace amounts of hydrocarbons in the glycol or polar phase. Water concentration in the polar phase was also analyzed using GC-3. However, in the case of benzene - MEG and water - MEG - benzene systems, the peak of benzene was very close (in time) to the peak of MEG both when GC-2 or GC-3 were used. Therefore both the glycol or polar (for the ternary system) and the hydrocarbon phase were analyzed using GC-1.

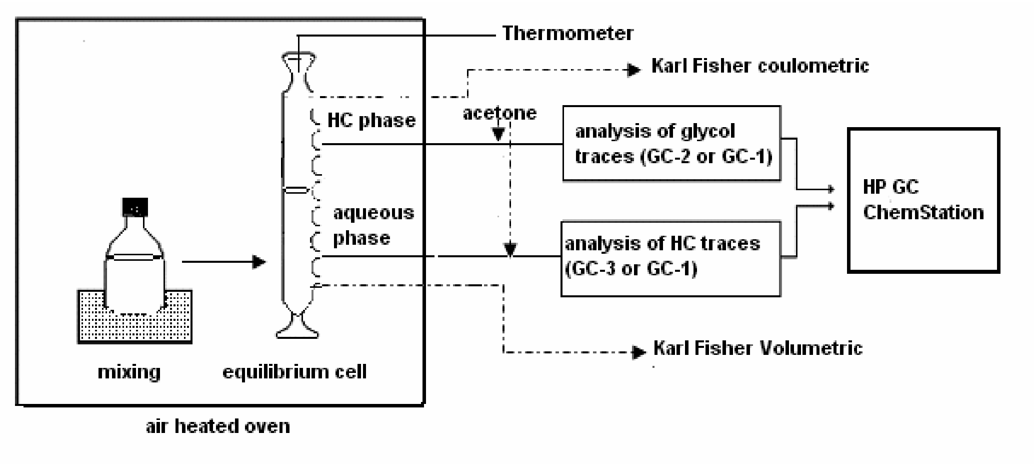

Figure 5.1. Sketch of the experimental procedure.

The water content in the hydrocarbon phase was obtained using Karl – Fisher titration, which is a method extensively used in chemical industry, providing very reliable results, especially for systems where the solubility of water in the hydrocarbon phase is very low such as the systems involved in this work. For comparison purposes the water content in the polar phase was obtained using Karl – Fisher (KF) titration in parallel to gas chromatography. Two different KF titration apparatus were used: Mettler Toledo DL37 Coulometric titrator for determining the amount of water in the HC phase and Mettler Toledo DL38 Volumetric titrator for determining the amount of water in the polar phase. Prior to analysis, external standards were analyzed in order to test the reliability of the measurements. The uncertainty of the water content measurements is estimated to be 4 % for the coulometric titrator and 1 % for the volumetric titrator. Regarding the polar phase, the results obtained using gas chromatography are in good agreement to those obtained with KF titration (deviation within the experimental uncertainty of each method). The values of the water content in the polar phase are those obtained using GC analysis. The experimental procedure is illustrated in Figure 5.1.

5.3. Experimental Results

Tables 5.3 and 5.4 present mutual solubility measurements for the binary and ternary systems studied, respectively. All the experimental measurements presented here contribute new data, for the following reasons: a) experimental data for the binary systems MEG - benzene are scarce and in most cases over a limited temperature range b) there are no measurements performed at low temperatures for the binary system MEG – toluene c) very few or no data for the binary systems TEG – benzene or toluene, d) there are no experimental data at all for the ternary systems presented in this work.

Table 5.2. Characteristics of the chromatographs used in this work.

	GC-1	**GC-2**	**GC-3**
Type	HP 5890, SERIES II	HP 5890, SERIES II	HP 6890
Column type	CP-Wax 52 CB polar capillary column	HP-PONA un-polar capillary column	CP-poraplot Q-HT
Column length	30 m	50 m	30m
Column i.d.	0.53 mm	0.2 mm	0.32mm
Column film thickness	1μm	0.5 μm	10μm
Injector type	7673	7673	7683
Injection volume	1.0 μL	0.2 μL	1.0 μL
Carrier gas	Helium	Helium	Helium
Detector type	FID	FID	TCD

FID: flame ionization detector
TCD: thermal conductivity detector

The results obtained in this work for the binary system of MEG - benzene are in excellent agreement with the solubility measurements of Staveley et al.[3],who measured the solubility of ethylene glycol in benzene using a synthetic method[a], as demonstrated in figure 5.7; however the

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[a] According to the method known masses of solute (from a weight pipette) and solvent were introduced into a glass tube, sealed and heated until the solution became homogeneous and then slowly cooled down. The temperature at which the two phases separated was determined as the cloud point.

solubility of benzene in MEG was not measured in by Staveley. Kugo et al.[4] on the other hand measured the solubility of benzene in MEG over a temperature range of 50 K, and their measurements are in very good agreement with the results obtained in this work. There is some disagreement regarding the reported solubility of benzene in MEG at the lower temperature measured by Kugo et al.[4] The work of Kugo et al.[4] indicates the formation of a closed loop at low temperatures, which was not observed in this work, even though solubility measurements were performed almost 30 K lower than the lowest temperature measurement of Kugo et al.[4].

Table 5.3. Mutual solubility measurements for the binary system glycol (1) + aromatic hydrocarbon, HC (2).

System	T/K	100 x_2 in glycol phase	100 x_1 in HC phase
Monoethylene glycol - benzene	279.2	4.664	0.106
	288.5	4.878	0.155
	303.3	5.005	0.299
	318.1	5.105	0.463
	332.6	5.530	0.753
	342.1	5.569	0.982
Monoethylene glycol - toluene	279.1	1.879	0.104
	297.9	2.014	0.211
	302.1	2.085	0.254
	312.1	2.188	0.320
	316.3	2.265	0.379
	323.2	2.382	0.470
	331.2	2.547	0.603
	345.1	2.808	0.957
	357.1	3.052	1.471
	361.0	3.170	1.671
Triethylene glycol - benzene	279.6	63.422	7.062
	281.6	64.375	7.222
	283.0	64.881	7.703
	284.3	65.926	8.045
	287.6	67.324	10.952
Triethylene glycol - toluene	279.0	30.839	1.074
	293.0	32.960	1.858
	302.0	34.780	2.265
	312.8	35.893	3.162
	321.2	38.138	4.159
	331.5	41.952	5.662
	344.2	46.375	8.366
	345.4	48.498	8.661

Finally, equilibrium measurements for the same system were performed by Zaretskii et al.[5]. Their results are in disagreement with all the other experimental works (including this one), especially regarding the solubility of MEG in benzene which is two orders of magnitude higher compared to the aforementioned studies.

Regarding the binary system of MEG - toluene, this work is in good agreement with the results obtained by Mandik et al.[6], as demonstrated in figure 5.2. In this work emphasis is given to low temperature measurements, which, combined with the work of Mandik et al. provide solubility data for a temperature range of more than 100 K. Hughes et al.[7] measured the system TEG - toluene using a synthetic method over a very limited temperature range, which is less than 15 K. Good agreement is obtained regarding the solubility of toluene in TEG, while the measured solubility of TEG in toluene at low temperatures is systematically lower than the one measured in this work.

5.4. Modeling results with the CPA EoS

The extension of CPA to systems containing aromatic hydrocarbons was already discussed in chapter 4; in order to account for the solvation between the associating and the aromatic compounds, an extra fitted parameter (*BETCR*) in the association term is used in addition to the binary interaction parameter (k_{12}) in the physical term (SRK term) for the mCR-1 combining rule. Accounting for the solvation is found to be highly important for systems containing glycols, since the use of only a binary interaction parameter (k_{12}) in the physical term cannot correlate simultaneously both solubilities. A typical result is presented in figure 5.3 for the system DEG – toluene system. The use of a single binary interaction parameter results in an underestimation of the DEG solubility in benzene of an order of magnitude.

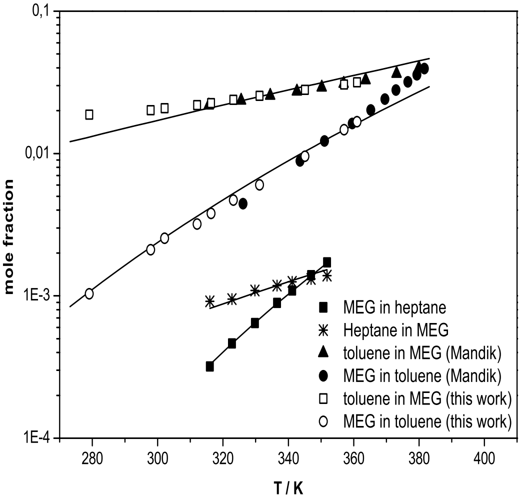

Figure 5.2. LLE data and correlation of MEG – toluene (k_{12}=0.051, BETCR=0.042) and MEG-heptane (k_{12}=0.047) systems. Experimental data for MEG – toluene are from this work and from Mandik and Lesek[6] while for MEG – heptane the experimental data are from Derawi et al.[1]

A physical evidence of the pronounced solvation between glycols and aromatics is provided by the increased solubilities compared to the homomorph aliphatic hydrocarbons. This is elucidated by figure 5.2, which presents LLE data for the systems MEG – heptane and MEG – toluene. The use of mCR-1 results in satisfactory calculations for the infinite dilution activity coefficients of toluene in MEG as can be seen in figure 5.4. Table 5.5 presents the correlation of the LLE of the binary systems involved in this study. For the correlation of the systems MEG + benzene and MEG + toluene all experimental data are considered, using only temperature independent interaction parameters.

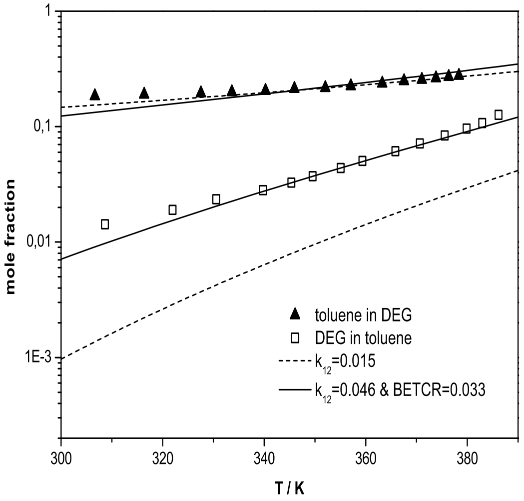

Figure 5.3. LLE correlation of DEG – toluene. Experimental data are taken from Mandik and Lesek[6].

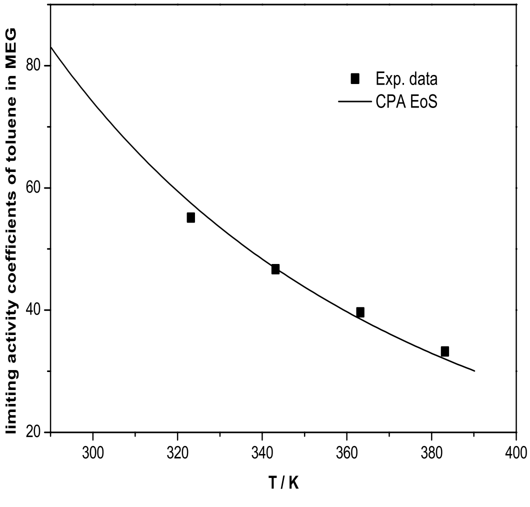

Figure 5.4. Limiting activity coefficients of toluene in MEG. Experimental data are from Zhang et al.[8].

Table 5.4. Mutual solubility measurements for the ternary systems of glycol (1) - water (2) - aromatic hydrocarbon, HC (3) at two different temperatures.

		Feed			Polar phase			HC phase		
System	**T / K**	**x_1**	**x_2**	**x_3**	**100 x_1**	**100 x_2**	**100 x_3**	**100 x_1**	**100 x_2**	**100 x_3**
MEG - water - benzene	298.2	0.1226	0.6340	0.2435	16.615	83.223	0.162	0.033	0.263	99.705
		0.1656	0.5711	0.2632	23.125	76.673	0.202	0.046	0.240	99.715
		0.2163	0.4972	0.2865	30.397	69.318	0.285	0.060	0.217	99.723
		0.2768	0.4090	0.3142	39.270	60.314	0.417	0.078	0.190	99.733
		0.4413	0.1691	0.3896	70.065	28.360	1.575	0.143	0.096	99.761
	323.2	0.1226	0.6340	0.2435	16.416	83.423	0.161	0.076	0.514	99.410
		0.1656	0.5711	0.2632	22.487	77.279	0.235	0.106	0.478	99.416
		0.2163	0.4972	0.2865	29.470	70.211	0.319	0.142	0.457	99.401
		0.2768	0.4090	0.3142	39.293	60.208	0.499	0.191	0.392	99.418
		0.4413	0.1691	0.3896	70.572	27.666	1.763	0.352	0.187	99.461
MEG - water - toluene	298.2	0.4316	0.2323	0.3361	64.746	34.555	0.700	0.134	0.094	99.772
		0.2907	0.4296	0.2797	41.494	58.272	0.234	0.080	0.159	99.761
		0.1725	0.5950	0.2325	22.455	77.494	0.051	0.038	0.220	99.742
		0.1273	0.6584	0.2144	15.167	84.807	0.027	0.023	0.245	99.732
	323.2	0.4316	0.2323	0.3361	64.438	34.696	0.866	0.330	0.197	99.474
		0.2907	0.4296	0.2797	42.687	57.013	0.300	0.214	0.320	99.466
		0.1725	0.5950	0.2325	21.672	78.255	0.073	0.105	0.438	99.457
		0.1273	0.6584	0.2144	15.942	84.019	0.038	0.069	0.472	99.460
TEG - water - toluene	298.2	0.2675	0.2480	0.4845	48.877	42.490	8.633	0.670	0.208	99.122
		0.1810	0.4384	0.3806	28.549	69.939	1.513	0.212	0.237	99.551
		0.0794	0.6620	0.2586	12.033	87.825	0.142	0.048	0.283	99.670
		0.0569	0.7115	0.2317	8.047	91.886	0.067	0.024	0.308	99.668
	323.2	0.2675	0.2480	0.4845	47.967	42.055	9.978	1.162	0.458	98.380
		0.1810	0.4384	0.3806	26.942	71.271	1.787	0.395	0.488	99.117
		0.0794	0.6620	0.2586	11.123	88.688	0.189	0.107	0.543	99.351
		0.0569	0.7115	0.2317	7.256	92.657	0.088	0.056	0.579	99.365

Table 5.5. LLE correlation results for the binary systems of glycol (1) + aromatic HC (2) with CPA EoS, expressed as %AAD of mole fraction (x) of the compound i.

I = Glycol – rich phase

II= Hydrocarbon – rich phase

					% AAD	**% AAD**
System	**Exp. T / K**	**Exp. Ref.**	k_{12}	**BETCR**	**x_2 in I**	**x_1 in II**
MEG – benzene	279.1–342.1	4, 5, this work	0.049	0.04	9.7	4.3
MEG – toluene	279.1–381.7	7, this work	0.051	0.042	9.7	11.5
DEG – benzene	293 – 353	9	0.028	0.035	10.6	36.3
DEG – toluene	306 – 386	6	0.046	0.033	9.5	7.7
TEG – benzene	279.6–287.6	this work	0.032	0.083	0.9	16.3
TEG – toluene	279.0-345.4	this work	0.038	0.048	7.5	3.6
Average					**8.8**	**12.7**

In all cases the correlative performance of the model is satisfactory, providing adequate calculations of mutual solubilities over extended temperature range, using temperature independent interaction parameters (k_{12} and BETCR). A typical example is the LLE correlation of MEG – toluene (presented in figure 5.2) which covers a temperature range of almost 100K.

The LLE correlation of the systems TEG - benzene and TEG - toluene is based on the experimental measurements obtained in this work. Gupta et al.[10] performed VLE measurements for both systems at atmospheric pressure and over a temperature range of almost 80 K. Prediction of VLE using the binary interaction parameters (k_{12} and *BETCR* in the case of systems with aromatic hydrocarbons) obtained from LLE is a demanding test of the model; CPA provides very satisfactory results, as illustrated by figures 5.5 and 5.6, enabling phase equilibria calculations (both VLE and the very demanding LLE) over a temperature range of more than 200 K.

The predictive performance of CPA for the ternary systems measured in this work is presented in Table 5.6. All calculations were performed based solely on interaction parameters obtained from the binary systems. For the binary systems of water - aromatic hydrocarbons and glycols - aromatic hydrocarbons the two adjustable parameters are temperature independent. For the MEG - water system the Elliott combining rule (ECR) with a binary interaction parameter k_{12}=-0.115 was used, since this was shown in chapter 2 to provide adequate results (both solid – liquid and vapour – liquid equilibrium) over an extended temperature range.

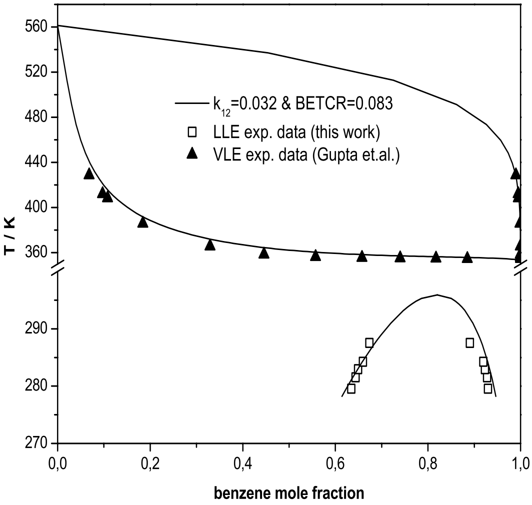

Figure 5.5. LLE and VLE correlation of TEG – benzene with CPA.

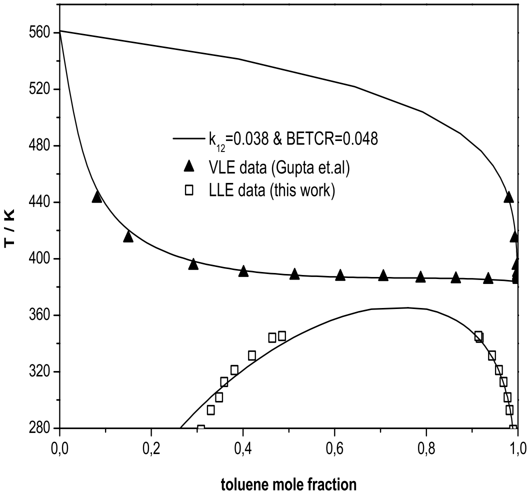

Figure 5.6. LLE and VLE correlation of TEG – toluene with CPA.

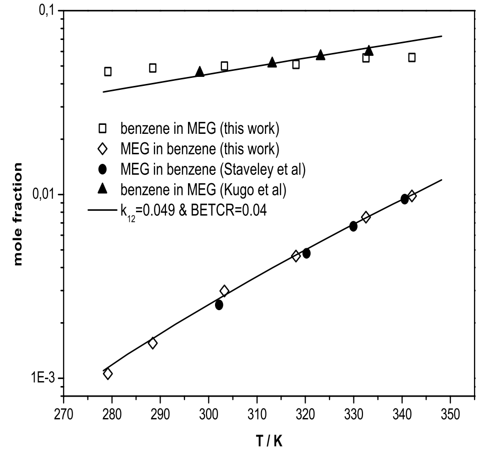

Figure 5.7. LLE correlation of MEG - benzene with CPA.

Derawi et al.[11] correlated the VLE of the binary system TEG - water, using both CR-1 and ECR. It was shown that the CR-1 combining rule performs better than ECR, providing in the temperatures tested an error of about 5 % in the vapour pressure. In the case of ECR, a much higher value of an interaction parameter is required and the error in vapour pressure is over 10 %. In this work both combining rules are tested for the TEG - water system, using the binary interaction parameters optimised at 297.6 K (i.e. CR-1 with k_{12}=-0.211 and ECR with k_{12}=-0.372, respectively). In all cases the binary parameters used are presented in Table 5.6, together with the percentage deviation (%AAD) of each compound of the ternary system in both phases.

As can be seen from Table 5.6, satisfactory predictions are achieved for all MEG containing systems with CPA at both temperatures. CPA adequately predicts even the “difficult” solubility of the hydrocarbon in the polar phase and the polar compounds in the hydrocarbon phase. The average deviations are 19 % for the prediction of the solubility of the aromatic hydrocarbon in the polar phase, 29 % for the solubility of glycol and 16 % for the solubility of water in the hydrocarbon phase, respectively. For the ternary system of TEG - water - toluene, the results obtained with ECR are inferior to those with CR-1 combining rule, which is probably due to the inferior correlation of the TEG - water binary system with ECR. Typical results are presented in Figures 5.8 – 5.10. Equally satisfactory is the prediction of the ternary system water - DEG - benzene at 298.15K as figure 5.11 shows. Johnson and Francis[2] however present equilibrium measurements (%wt fraction) only for one phase and consequently the distribution coefficient of MEG cannot be calculated based on these experimental data. CPA, however, predicts satisfactory the ratio of benzene/water as a function of water weight fraction.

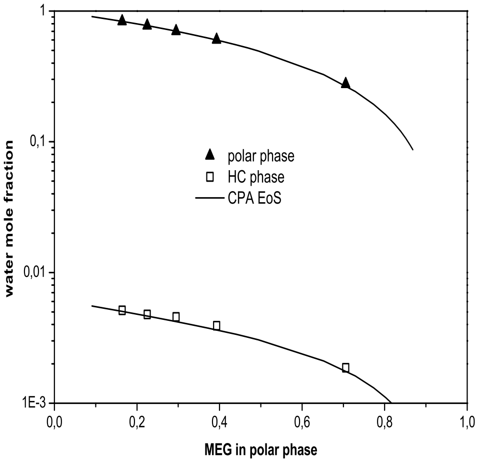

Figure 5.8. Prediction of water solubility in the polar and the hydrocarbon phase for the ternary system MEG - water - benzene at 323.2 K with CPA.

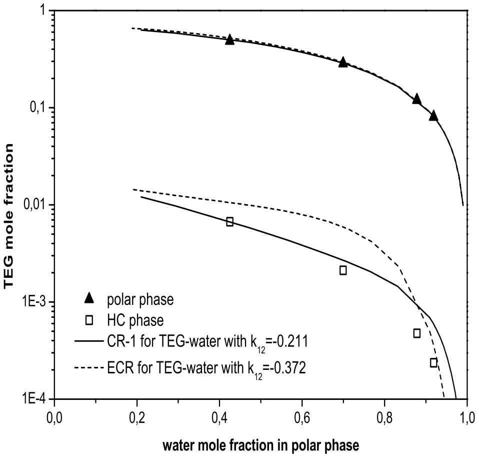

Figure 5.9. Prediction of TEG solubility in the polar and HC phases for the ternary system TEG - water - toluene at 298.2 K. The solid line is with CR-1 and k_{12}=-0.211 for the water - TEG binary system; the dashed line is with ECR and k_{12}= -0.372 for the water - TEG system.

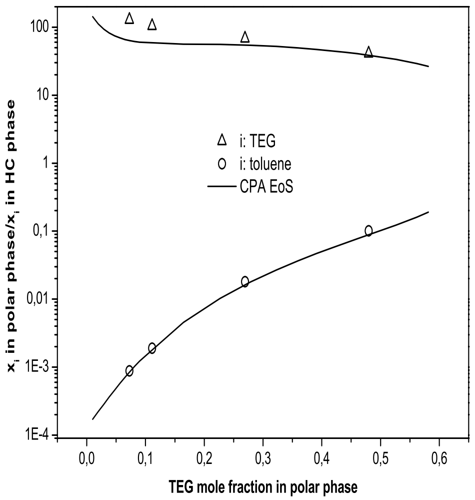

Figure 5.10. Prediction of the partition coefficients of TEG and toluene for the ternary system TEG - water - toluene at 323.2 K using CR-1 with k_{12}=-0.211 for the water - TEG system.

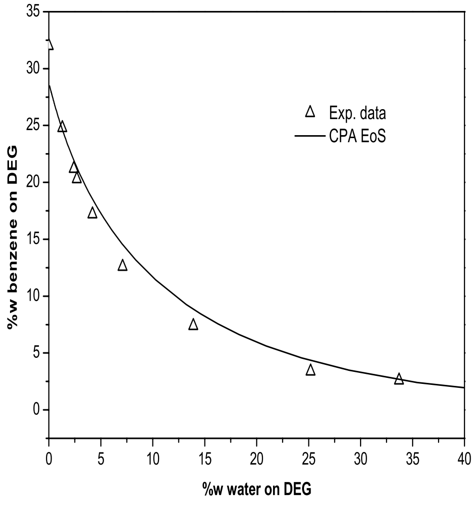

Figure 5.11. Prediction of %wt of benzene as a function of %wt of water on DEG for the ternary system DEG - water - benzene at 298.15 K. Experimental data from Johnson and Francis[2].

Table 5.6. LLE prediction results for the ternary systems of glycol (1) - water (2) - aromatic hydrocarbon (3) with CPA, expressed as %AAD of mole fraction (x) of the compound i in each phase.

			%AAD in polar phase			**%AAD in HC phase**		
System	**T / K**	**Interaction parameters**	**x_1**	**x_2**	**x_3**	**x_1**	**x_2**	**x_3**
MEG - water - benzene	298.2	k_{12}=-0.115 & ECR, k_{13}=0.049 & BETCR=0.04, k_{23}=0.0355 & BETCR=0.079	1.9	1.5	19.4	17.5	11.9	0.01
	323.2	k_{12}=-0.115 & ECR, k_{13}=0.049 & BETCR=0.04, k_{23}=0.0355 & BETCR=0.079	1.3	1.1	24.8	16.1	5.2	0.01
MEG - water - toluene	298.2	k_{12}=-0.115 & ECR, k_{13}=0.051 & BETCR=0.042, k_{23}=0.0095 & BETCR=0.06	2.5	1.1	20.6	22.5	19.3	0.03
	323.2	k_{12}=-0.115 & ECR, k_{13}=0.051 & BETCR=0.042, k_{23}=0.0095 & BETCR=0.06	1.8	0.7	13.3	7.5	11.0	0.03
TEG - water - toluene	298.2	k_{12}=-0.211 & CR-1, k_{13}=0.038 & BETCR=0.048, k_{23}=0.0095 & BETCR=0.06	5.3	2.3	23.6	59.0	29.9	0.06
	323.2	k_{12}=-0.211 & CR-1, k_{13}=0.038 & BETCR=0.048, k_{23}=0.0095 & BETCR=0.06	2.6	1. 8	11.4	50.6	17.6	0.04
	298.2	k_{12}=-0.372 & ECR, k_{13}=0.038 & BETCR=0.048, k_{23}=0.0095 & BETCR=0.06	5.4	3.2	66.6	75.7	41.3	0.2
	323.2	k_{12}=-0.372 & ECR, k_{13}=0.038 & BETCR=0.048, k_{23}=0.0095 & BETCR=0.06	2.8	3.0	58.5	82.8	28.6	0.4
Average (all systems and conditions)			**2.9**	**1.8**	**29.3**	**40.0**	**19.9**	**0.1**

5.5. Comparison of CPA to PVTsim v.14

State of the art models, which are commonly used by industrial simulators, are among the main tools for phase equilibria calculations of such types of complex systems in industry. Even when reliable in-house models exist, industrial simulators are in general also used for comparison purposes. In an attempt to demonstrate the importance of explicitly accounting for association/solvation, the performance of CPA EoS is compared to the commercial simulator PVTsim v.14 of Calsep AS. Binary and ternary systems of MEG with aromatic hydrocarbons are considered.

PVTsim uses SRK with HV mixing rules for MEG – water binary mixture, which is already presented in chapter 1. A modified, however, expression for the characteristic energy parameters ($g_{ji} - g_{ii}$ and $g_{ij} - g_{jj}$) is used[12], increasing the total number of adjustable parameters per binary system to 5, compared to the 3 parameters used in the traditional HV expressions. The results for MEG – water system are similar to CPA in terms of calculated activity coefficients. For all binary mixtures of water – aromatic or glycol – aromatic hydrocarbons, however, the model simply reduces to SRK with classical Van der Waals mixing rules (due to lack of HV parameters), which fails to correlate both solubilities with the same interaction parameter (k_{12}). In many cases default binary interaction parameters (k_{12}) are used as for example k_{12}=0.5 for water – aromatic systems. In this section for all binary systems and when the SRK EoS is used, the binary interaction parameters are for consistency fitted to experimental data. Such a task is not very straightforward since SRK systematically fails to correlate both solubilities using the same binary parameter. A typical result for the system MEG – benzene is shown in figure 5.12. SRK erroneously calculates that the solubility of benzene in the polar phase is lower compared to the solubility of MEG in the hydrocarbon phase, which is opposite to the experimental trend. By fitting the solubility of MEG in the hydrocarbon phase, the solubility of benzene in the polar phase is underestimated by two orders of magnitude. Similar observations are made for water – aromatic hydrocarbon systems, in the case of which, SRK EoS significantly underestimates the solubility of the aromatic hydrocarbon in the aqueous phase, when the binary interaction parameter is fitted to the industrially important water solubility in the hydrocarbon phase.

Since the calculation of the solubility of the aromatic hydrocarbon in the polar/aqueous phase is in error for the binary systems, the prediction of the solubility of the hydrocarbon in the ternary system is also in error. Figures 5.13 and 5.14 present a typical comparison of the predictive performance of CPA and PVTsim for the ternary system MEG – water – benzene at 298.15K. For PVTsim calculations, the binary interaction parameters for water – benzene and MEG – benzene systems are fitted to LLE data, in the same way as with CPA. For water – benzene the interaction parameter used is k_{12}=0.28 while for MEG – benzene the value of k_{12}=0.128 is used. For MEG – water the default five binary interaction parameters of the HV mixing rule are used.

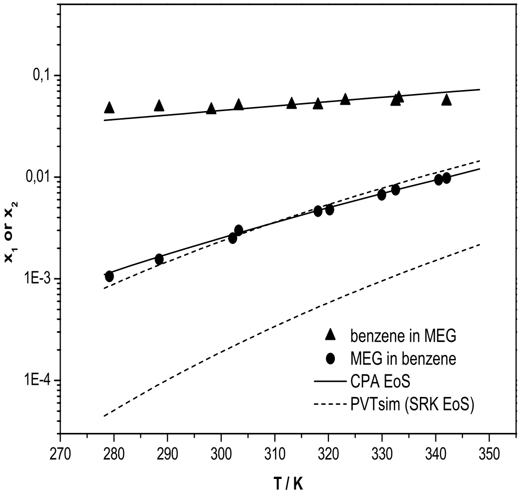

Figure 5.12. LLE correlation of MEG – benzene using CPA (k_{12}=0.049 and BETCR=0.04) and PVTsim (SRK EoS with k_{12}=0.128).

Although the prediction of the solubility of water and MEG in both the polar and the hydrocarbon phase is similar with both models, as typically demonstrated in figure 5.13 for the water solubility, the prediction of the solubility of benzene in the polar phase is strongly underestimated, resulting in an underestimation of the partition coefficient of toluene as demonstrated by figure 5.14. This behaviour is typical also for the other ternary systems studied, suggesting that reliable predictions require models that adequately account for the physics of all binary systems, such as the solvating effects between aromatic hydrocarbons and water and glycols.

The use of PVTsim cannot demonstrate the capabilities of the local composition concept because it is not used for all binary systems where solvating/associating occurs. However the successful application of the local composition concept for MEG – water evidences that such a concept could be an alternative towards Wertheim's theory. For this reason a detailed comparison of the two approaches is presented in chapter 6.

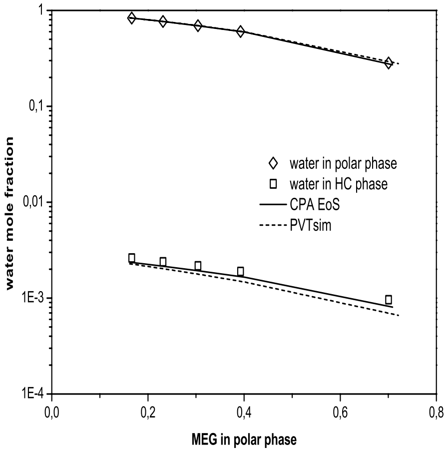

Figure 5.13. Prediction of water mole fraction between the polar and the hydrocarbon phase for the ternary system water – MEG – benzene at 298.15K using CPA and PVTsim.

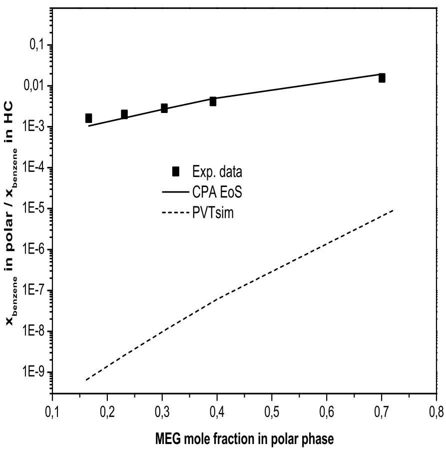

Figure 5.14. Prediction of benzene distribution coefficients between the polar and the hydrocarbon phase for the ternary system water – MEG – benzene at 298.15K using CPA and PVTsim.

5.6. Conclusions

In this work experimental measurements of binary and ternary systems containing glycols, aromatic hydrocarbons and water are presented. Gas chromatography and Karl Fisher titration were used to analyse the traces of the components in each phase. The results obtained in this work are in good agreement with other experimental data, for the temperature range that comparison was possible, demonstrating the reliability and validity of the measurements.

The CPA EoS was used to correlate the binary systems and predict the ternary based solely on temperature independent binary parameters. The LLE correlative performance of the model is very satisfactory over extensive temperature ranges, while the same parameters can be used for VLE predictions. Adequate predictions can be achieved in the case of the ternary systems at different temperatures, based on common and temperature independent binary interaction parameters.

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Chapter 6.

Phase Equilibria of Systems with MEG as Hydrate Inhibitor. Results with CPA and an EoS/G^E Model.

6.1. Introduction

It is well known that classical cubic equations of states (EoS) fail to represent the phase behavior of mixtures of polar and non-polar compounds in water. Water is often handled by assuming binary interaction coefficients of the order of 0.5 for the hydrocarbon-water interactions. At usual pipeline conditions, this assumption will somewhat underestimate the solubility of water in hydrocarbon liquid phases and give a completely incorrect picture of the solubility of hydrocarbons in the aqueous phase. If the pipeline fluid also contains a hydrate inhibitor, this assumption may have a very significant impact on the phase behavior and more probably will lead to poor results for water – hydrocarbon – inhibitor mixtures.

In this chapter we compare two models which are capable of describing mixtures of polar and non-polar compounds and which also, by proper parameterization, can reduce to classical cubic Equations of State. One of these models is the CPA EoS which explicitly accounts for hydrogen bonding by incorporating the association term from the SAFT family. The model is already shown to adequately describe LLE or VLLE of water – hydrocarbons including also the solubility of hydrocarbon in the aqueous phase (see chapter 4), LLE of glycol – hydrocarbon systems (Derawi et al.[1] and chapter 5) as well as VLE and SLE of water – glycol systems (Derawi et al.[2] and chapter 3). The alternative approach considered in this chapter is the use of an EoS/G^E model. Here, the SRK EoS with the Huron – Vidal mixing rule[3] using the modified NRTL model[3] is used for the following reasons: (i) successful applications of the model for industrially important systems containing methanol as hydrate inhibitor have been presented[4] (ii) the model reduces to the classical SRK mixing rule, if the parameters are appropriately selected. Both models are already presented in details in chapter 1 of the thesis.

In this work the two models are evaluated based on existing experimental data of binary systems containing water or glycols and hydrocarbons, including both aliphatics and aromatics. Finally the predictive performance of the models is evaluated based on multicomponent systems containing MEG.

6.2. Liquid – liquid equilibria of binary water – hydrocarbon and MEG – hydrocarbon systems

The first part of this work presents a comparison of the correlative performance of CPA and SRK/HV based on experimental data for binary aqueous systems, including both aliphatic as well as aromatic hydrocarbons. Regarding the SRK/HV EoS, the (three) parameters per binary system originally proposed by Pedersen et al.[4] for water – aliphatic hydrocarbons are used. In order to improve the predictions for high temperatures Pedersen et al.[5] suggested a new expression for the interaction parameters g_{ji} and g_{ij}, for binary systems of H_2O with one of the components N_2, CO_2, C_1, C_2, C_3 or n-C_4. This temperature dependent approach increases the number of adjustable parameters to 5 per binary system.

Based, however, on the previously presented satisfactory performance of SRK/HV with three adjustable parameters[4] for multicomponent systems and on the need of keeping the number of adjustable parameters as low as possible, the former approach is used in this work for all binary systems. For water – hydrocarbon systems the SRK/HV energy parameters are presented in table 6.1; for glycol – hydrocarbon binary systems the three adjustable parameters of SRK/HV, obtained in this work, are presented in tables 6.2 and 6.3, respectively.

Table 6.1. Interaction energy parameters for binary mixtures of water and an indicated second component with SRK/HV.

2nd component	**Reference**	$g_{12}-g_{22}/R$ **[K]**	$g_{21}-g_{11}/R$ **[K]**	α_{12}
Methane	4	410	2291	0.15
Propane	4	847	2650	0.15
n-butane	4	793	2501	0.15
n-hexane	4	1187	2878	0.15
n-heptane	4	-81	2741	0.15
n-octane	This work	4272	2520	0.25
n-decane	This work	-228	2690	0.14
Benzene	This work	591	1998	0.175
Toluene	This work	535	2031	0.17
Ethyl-benzene	This work	641	1908	0.17
m-xylene	This work	282	2023	0.17
1-hexene	This work	2729	2401	0.24
1-decene	This work	793	2389	0.16

Table 6.2. Interaction energy parameters for binary mixtures of MEG and an indicated second component with SRK/HV.

2^{nd} **component**	**Reference**	$g_{12}-g_{22}/R$ **[K]**	$g_{21}-g_{11}/R$ **[K]**	α_{12}
Methane	This work	181	2274	0.07
n-hexane	This work	1249	2553	0.20
n-heptane	This work	430	2595	0.13
Benzene	This work	13	1927	0.15
Toluene	This work	726	1624	0.27
Water	This work	105	59	0.95

Table 6.3. Interaction energy parameters for binary mixtures of TEG and an indicated second component with SRK/HV.

2^{nd} **component**	**Reference**	$g_{12}-g_{22}/R$ **[K]**	$g_{21}-g_{11}/R$ **[K]**	α_{12}
n-heptane	This work	143	2157	0.06
Benzene	This work	15	809	0.16
Toluene	This work	45	1091	0.15

For CPA, the adjustable parameter of the model (k_{ij}) for the binary systems of water – aliphatic hydrocarbons is obtained based on the correlation presented in chapter 4. Successful correlation of LLE or VLLE of binary water – aromatic hydrocarbon systems requires an additional parameter (*BETCR*) in the expression of the cross – association strength, while the binary interaction parameter in the physical term (k_{ij}) can be obtained from the homomorph aliphatic hydrocarbon. The interaction parameters used for CPA calculations in this work are presented in table 6.4.

The following summarize our observations for water – hydrocarbon systems:

1. For both aliphatics and aromatics, SRK/HV does not represent the temperature dependency of the water solubility as well as the CPA EoS. A typical plot is presented in figure 6.1 for water – benzene, showing that CPA correlates better the industrially important solubility of water in the hydrocarbon phase compared to SRK/HV. Table 6.5 summarizes the correlative performance of SRK/HV and CPA EoS for water – hydrocarbon systems.

2. The opposite is observed for the hydrocarbon solubility in the aqueous phase, where SRK/HV performs systematically better than CPA. In particular CPA significantly overestimates the solubility of n-decane and 1-decene in the aqueous phase, compared to the

correlation results of the other binary systems, for reasons that are already discussed previously (chapter 4).

3. Pedersen et al.[4] followed an optimization procedure where the SRK/HV parameters were optimized based on the concentration of both components in each phase. Given, however, the importance of the water solubility for the oil industry, SRK/HV parameters could be in principle explicitly fitted to experimental water solubilities in the hydrocarbon phase. This procedure can, however, introduce significant errors in the calculated solubility of the hydrocarbon in the aqueous phase, as typically presented by figure 6.2 for water – toluene. Setting in the optimization a higher weight for the water solubility in the hydrocarbon phase results a similar behaviour to the one obtained when both solubilities are equally weighted. As a result, SRK/HV parameters are optimized also in this work based on both solubilities, as was done by Pedersen et al.[4]. The objective function used during the optimization procedure is the following:

$$OBJ = \ln\left(\frac{x_{11,cal}x_{12,cal}}{x_{11,\exp}x_{12,\exp}}\right)^2 + \ln\left(\frac{x_{21,cal}x_{22,cal}}{x_{21,\exp}x_{22,\exp}}\right)^2$$

where $x_{i,j}$ refers the solubility of component i in the phase j.

4. The parameters presented by Pedersen[4] for water – n-alkanes (see table 6.1) suggest that the value of the parameter α_{12} was kept constant during the optimization to the fixed value of α_{12}=0.15**.** Initially this procedure was also followed for the optimized parameters of this work. It was found, however, that a simultaneous optimization of all three parameter leads to better results for some binary systems. For example, the optimized parameters for water – n-octane with α_{12}=0.15 (fixed) are $g_{12} - g_{22} / R$=1028 and $g_{21} - g_{11} / R$=2092. This set of parameters results in %AAD=143 for the water solubility in the hydrocarbon phase and 42.5 for the n-octane solubility in water. On the contrary, the parameters presented in table 6.1 (all fitted simultaneously) provide an overall better correlation as can be seen in table 6.5.

5. It is worth mentioning that a single binary interaction parameter with CPA suffices for correlating both solubilities for water – aliphatic hydrocarbons. The solubility of water in the hydrocarbon phase can be reasonably represented with CPA for most binary water – aliphatic hydrocarbon systems even with k_{12}=0 (pure predictions). The use of a binary interaction parameter is due to the simultaneous fitting of the solubility of hydrocarbon in

the water phase. Furthermore, in the case of water – aromatics, the parameters are optimized based on both solubilities, using the same objective function as for SRK/HV.

6. SRK/HV with selected parameters captures the minimum in the solubility of hydrocarbon in the aqueous phase, both for water aliphatics as well as for water – aromatics. This is also a reason to attribute the superior correlation of the hydrocarbon solubility in the aqueous phase, compared to CPA EoS. This is a remarkable observation, in the sense that simple models are not expected to predict the experimentally observed minimum in the solubility of hydrocarbons in water. However, SRK/HV with three parameters cannot adequately capture the temperature dependency of the hydrocarbon solubility at increased temperatures and pressures.

Another key system of this study is the binary water – MEG, especially having in mind the importance of multicomponent multiphase equilibrium in mixtures with MEG as hydrate inhibitor. Typical VLE correlation results are demonstrated in figure 6.3, at two different temperatures and pressures. For CPA, it was shown that ECR using a binary interaction parameter k_{12}=-0.115 can correlate both SLE and VLE of the system. Derawi et al.[2] presented correlation results of the system at two temperatures (343.15 and 363.15K). In this work the same binary interaction parameter is used to predict VLE at higher temperatures up to 383.15K, providing satisfactory results (error less than 4.5% in vapor pressure). Equally good, and occasionally better, is the performance of SRK/HV model, using the parameters tabulated in table 6.2, which have been obtained by simultaneous fitting of VLE data as well as infinite dilution activity coefficient data of MEG in water. Infinite dilution activity coefficient data were used because of the several sets of parameters that equally well fitted VLE data. The suggested set of parameters has a value of α_{12}=0.95, which is relatively high compared to all the other values presented in tables 6.1 – 6.3. Renon and Prausnitz[18] suggest that the non-randomness parameter α_{12} could be related to the co-ordination number z, which is of the order of 6-12; hence the value of the non-randomness parameter α_{12} should not exceed 0.3, in order to have some physical meaning. Nevertheless, the authors[18] still support the fact that this parameter should just be treated as an empirical one. The high value of α_{12} for MEG – water seems to be related to the highly polar/associating mixture and is justified by the empirical character of the parameter. Pedersen et al.[4] report a value of α_{12}=1.2 for the highly polar methanol – water system, which further supports the proposed value for MEG – water.

Pedersen et al.[4] concluded that for water and methanol the use of a Mathias – Copeman expression for the energy parameter of the pure compounds provides superior results, compared to the classical SRK energy expression. The same is the case for MEG; the Mathias – Copeman parameters for MEG are taken from Derawi et al.[2] while for water the parameters from Pedersen[4] are used.

Table 6.4. Binary interaction parameters used for the CPA EoS.

Binary system	Reference	k_{12}	BETCR
MEG – water	2,chapter 2	-0.115 & ECR	-
MEG – methane	This work	0.134	-
MEG – hexane	1	0.059	-
MEG – heptane	1	0.047	-
MEG – benzene	Chapter 5	0.049	0.04
MEG – toluene	Chapter 5	0.051	0.042
TEG – hexane	1	0.094	-
TEG – benzene	Chapter 5	0.032	0.083
TEG – toluene	Chapter 5	0.038	0.048
Water – methane	2	-0.045	-
Water – propane	Chapter 4	0.1135	-
Water – hexane	Chapter 4	0.0355	-
Water - benzene	Chapter 4	0.0355	0.079
Water – toluene	Chapter 4	0.0095	0.06

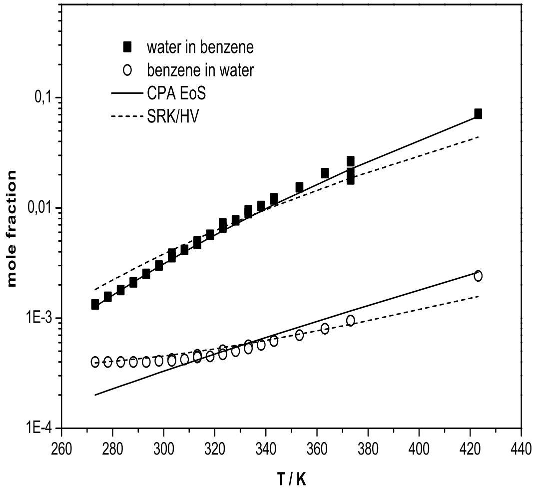

Figure 6.1. LLE correlation of water – benzene with CPA and SRK/HV. Experimental data are from Tsonopoulos and Wilson[6], Chen and Wagner[7] and Sørensen and Arlt[8].

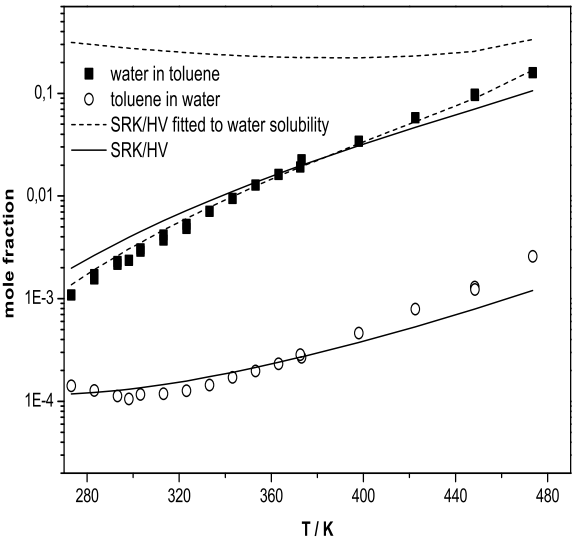

Figure 6.2. LLE correlation of water – toluene with SRK/HV using two different sets of energy interaction parameters. The dashed line is when parameters are optimized based on both solubilities (parameters presented in table 6.1) and the solid line is when the parameters ($g_{12}-g_{22}/R$=277, $g_{21}-g_{11}/R$ =2058, α_{12} =0.38) are optimized based on water solubility data in the HC phase. Experimental data are from Sørensen and Arlt[8], Anderson and Prausnitz[11], Chen and Wagner[12].

For MEG – methane there are several data[9,10] for the solubility of methane in MEG at different temperatures and pressures up to 400bar, but no data, to the best of our knowledge, for the solubility of MEG in the gas phase. Both CPA and SRK/HV correlate very satisfactorily the solubility of MEG at several temperatures. Although the binary interaction parameter used with CPA is relatively high (k_{12}=0.134), it is constant at various temperatures. On the other hand SRK EoS cannot correlate the system using a constant binary interaction parameter. For satisfactory calculations with SRK, a temperature dependent binary interaction parameter should be used (k_{12}=0.001*T-0.2362).

Table 6.5. Percentage Average Absolute Deviation (% AAD) between experimental and calculated water solubilities in the hydrocarbon phase (X_{water}) or the vapor phase (y_{water}) and hydrocarbon solubilities in the aqueous phase (X_{HC}).

Hydrocarbon	T range /K	%AAD in X_{water}		%AAD in X_{HC}		%AAD in y_{water}	
		SRK/HV	CPA	SRK/HV	CPA	SRK/HV	CPA
propane	278 – 366	31.4	3.4	18.3	35.9	4.8	4.1
butane	310 – 420	65.7	11.7	24.5	26.5	8.4	9.5
n-hexane	280 – 473	44.1	11.9	43.0	31.1	-	-
n-octane	310 - 550	48	9.7	64.2	44.1	6.7	1.9
n-decane	290 – 566	51	8.2	12.2	264	-	-
Benzene	273 - 473	18.2	5.3	10.4	19.5	-	-
Toluene	273 – 473	33.2	5.1	18.7	23.5	-	-
Ethylbenzene	303 - 568	77.4	6.5	9.6	47.1	1.9	1.1
m-xylene	373 - 473	26.0	3.7	9.4	8.3	-	-
1-hexene	310 - 496	29.3	7.6	33.8	29.3	7.4	1.2
1-decene	310 - 550	30.9	12.7	52.6	288	-	-
Average		**40.9**	**7.5**	**25.4**	**72.5**	**5.8**	**3.6**
Average[b]		**40.8**	**6.9**	**23.9**	**29.6**	**5.8**	**3.6**

The last part of this section focuses on the correlation of LLE of glycol – hydrocarbons. Among glycols, MEG and TEG are considered, since these are of great interest to the oil and gas industry. Like MEG a Mathias – Copeman expression for the energy parameter is used also for TEG with SRK/HV; the values are obtained from Derawi et al.[2]. For comparison reasons the performance of the CPA EoS is also presented. SRK/HV with three binary energy parameters correlates very satisfactorily the LLE of glycol – hydrocarbons over a limited temperature range. This is the case for MEG – hexane, TEG – heptane and TEG – benzene binary systems, as demonstrated in table 6.6. However, in the case of extensive temperature ranges, such as MEG – heptane (when aliphatic hydrocarbons are considered), or in the case of aromatics hydrocarbons where the temperature range is even greater, SRK/HV cannot follow the temperature dependency of both solubilities with the same success. SRK/HV correlates better the solubility of aromatic hydrocarbons in the glycol phase, but for the solubility of glycol in the hydrocarbon phase the results are inferior compared to CPA. Typical results are presented in figure 6.4 for MEG – n-hexane and figure 6.5 for MEG – toluene system.

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[b] This is the average error without including the systems water – n-decane and water – 1-decene

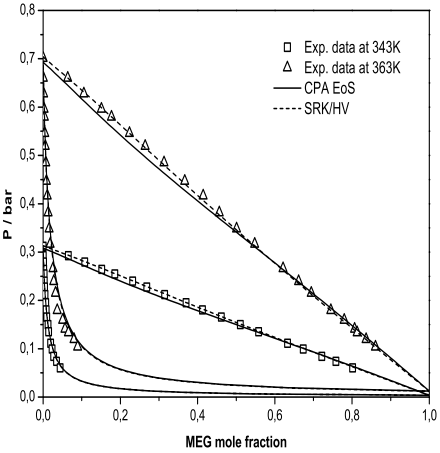

Figure 6.3. VLE correlation of water – MEG binary system at 343K and 363K with CPA and SRK/HV. Experimental data from Chiavone-Filho et.al.[13]

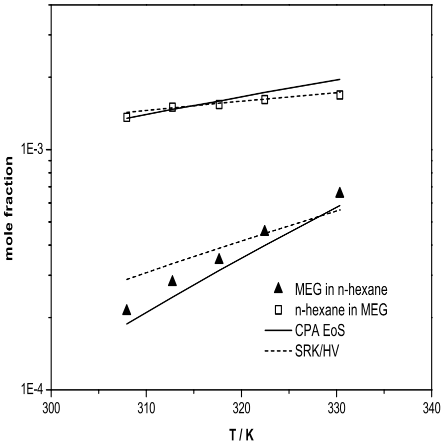

Figure 6.4. LLE correlation of MEG – hexane system with CPA and SRK/HV. Experimental data are taken from Derawi et al.[14]

Table 6.6. LLE correlation results for the binary systems of glycol (1) + hydrocarbon (2) with SRK/HV and CPA EoS, expressed as %AAD of mole fraction (x) of the compound i.

I = Glycol – rich phase

II= Hydrocarbon – rich phase

		% AAD x_2 in I		**% AAD x_1 in II**	
System	**Exp. T range / K**	**SRK/HV**	**CPA**	**SRK/HV**	**CPA**
MEG – n-hexane	308 – 330	2.0	5.9	16.6	11.5
MEG – n-heptane	316 – 352	6.7	5.3	21.2	1.2
MEG – benzene	279 – 342	3.3	9.7	22.4	4.3
MEG – toluene	279 – 382	2.9	9.7	43.4	11.5
TEG – n-heptane	309 – 351	4.7	4.6	14.2	4.7
TEG – benzene	279 – 288	0.2	0.9	9.6	16.3
TEG – toluene	279 – 345	2.8	7.5	23.4	3.6
Average		**3.2**	**7.4**	**26.6**	**7.7**

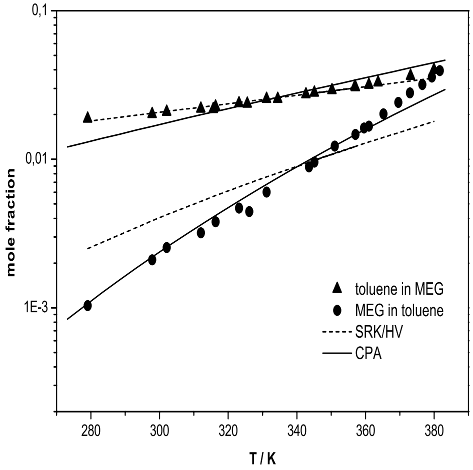

Figure 6.5. LLE correlation of MEG – toluene system with CPA and SRK/HV. Experimental data are taken from chapter 5 of the thesis and Mandik et al.[15]

6.3. Prediction of multicomponent multiphase equilibria of systems containing MEG.

The prediction of multicomponent multiphase equilibrium based solely on interaction parameters obtained from binary data can be a demanding test for the performance of a thermodynamic model. In this section the predictive performance of CPA and SRK/HV is tested for mixtures containing water, MEG and aliphatic as well aromatic hydrocarbons. These mixtures are of importance to the oil industry due to the extensive use of MEG as gas hydrate inhibitor. For the multicomponent mixtures considered in this work, it is often the case that literature data are available at various T and P conditions; hence for the CPA EoS, all calculations are based on common and temperature independent binary interaction parameters. Since both models reduce to the classical SRK for mixtures of hydrocarbons, no binary interaction parameters are used for hydrocarbons. Finally, for MEG – propane, due to lack of binary data, no interaction parameters are used for both models. Prediction results with the two models are presented in tables 6.7-6.12. The following summarize our observations:

1. For the ternary systems of MEG – water – aromatic hydrocarbons (results presented in tables 6.7 and 6.8), the performance of CPA is superior to SRK/HV for the prediction of the

solubility of MEG in the hydrocarbon phase. This could be attributed to the inferior correlation with SRK/HV of MEG solubility in the case of binary MEG – hydrocarbon. A similar conclusion can be obtained for the solubility of water in the hydrocarbon phase, which also seems to be influenced by the inferior correlation of the water solubility in the hydrocarbon phase, when SRK/HV is used. Typical results are presented in figure 6.6, for the ternary system MEG – water – benzene.

2. Similar conclusions can be drawn in the case of the quaternary system MEG – water – methane – toluene (table 6.10) and the five component systems MEG – water – methane – propane – toluene (table 6.11) and MEG – water – methane – propane – n-heptane (table 6.12), where the predicted solubilities of MEG and water in the HC liquid phase are systematically better with CPA. Typical results are presented in figure 6.7 for MEG – water – methane – toluene.

3. Although the solubility of the aromatic HC's in MEG are correlated better with SRK/HV compared to CPA, the predicted solubility of the aromatic hydrocarbon in the polar phase is equally accurate and occasionally better obtained with CPA, not only for the ternary systems presented in tables 6.7 and 6.8, but also for the quaternary or five-component systems presented in tables 6.10 and 6.11. This could be attributed to the correct representation of the solvation with CPA, compared to the local composition concept which seems to be more sensitive compared to the association term.

4. Regarding the prediction of the solubility of water and MEG in the vapour phase, the performance of the two models is overall similar. In some cases SRK/HV performs better than CPA and vice versa. Due to the very small amounts of these components present in the gas phase (and especially the MEG content with is usually less than 10 molar ppm) no definite conclusions can be extracted. It is worth mentioning that, in several cases for multicomponent systems considered in this work, the MEG solubility in the gas phase has not been measured. Similar observations can be made for the solubility of n-heptane in the polar phase for the five-component system MEG – water – methane – propane – n-heptane, with an experimental value of 2 ppm(mol) at 283K and 2 – 5 ppm(mol) at 310K. Although SRK/HV overestimates the n-heptane solubility of an order of magnitude, both due to the very low solubility as well as to the use of no binary interaction parameters for MEG – propane (which influences the calculated n-heptane solubility), no definite conclusions can be made.

Table 6.7. LLE prediction of the ternary system MEG – water –benzene with CPA and SRK/HV, expressed as % AAD. The binary parameters are presented in table 6.4 for the CPA EoS and in tables 6.1 and 6.2 for the SRK/HV.

		Polar phase % AAD		HC phase % AAD	
Compound	**T / K**	**CPA**	**SRK/HV**	**CPA**	**SRK/HV**
MEG	298	1.9	1.9	17.5	33.5
Water	298	1.5	1.5	11.9	15.0
Benzene	298	19.4	18.8	~0	~0
MEG	323	1.3	1.3	16.1	2.7
Water	323	1.1	1.1	5.2	3.9
Benzene	323	24.8	16.6	~0	~0
		Average %AAD for all temperatures			
MEG		**1.6**	**1.6**	**16.8**	**18.1**
Water		**1.3**	**1.3**	**8.5**	**9.4**
Benzene		**22.1**	**17.7**	**~0**	**~0**

Table 6.8. LLE prediction of the ternary system MEG – water – toluene with CPA and SRK/HV EoS, expressed as % AAD. The binary parameters are presented in table 6.4 for the CPA EoS and in tables 6.1 and 6.2 for the SRK/HV.

		Polar phase % AAD		HC phase % AAD	
Compound	**T / K**	**CPA**	**SRK/HV**	**CPA**	**SRK/HV**
MEG	298	2.5	2.5	22.5	118
Water	298	1.1	1.1	19.3	44.4
Toluene	298	20.6	26.6	~0	0.1
MEG	323	1.8	1.8	7.54	31. 6
Water	323	0.7	0.8	11.01	29.3
Toluene	323	13.3	21.1	~0	0.1
		Average %AAD for all temperatures			
MEG		**2.2**	**2.2**	**15.0**	**74.8**
Water		**0.9**	**0.9**	**15.2**	**36.9**
Toluene		**17.0**	**23.9**	**~0**	**0.1**

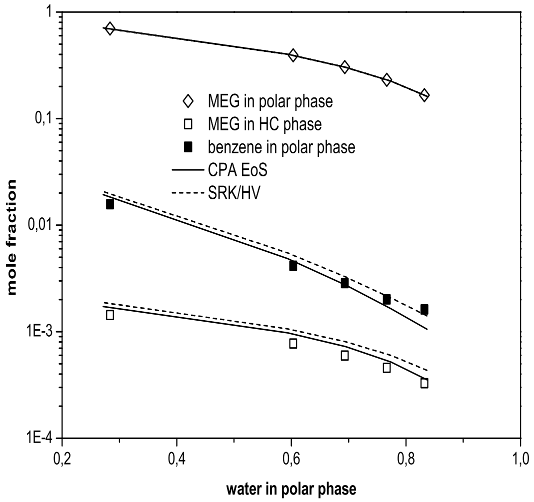

Figure 6.6. Prediction of the solubility of MEG in the polar and the HC phase with the CPA and SRK/HV EoS, for the ternary system MEG – water – benzene at 298.2K.

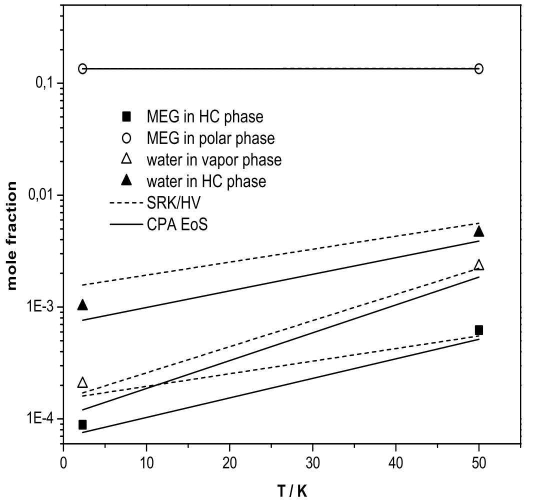

Figure 6.7. Prediction of MEG solubility in the polar and liquid HC phase and water solubility in vapour and liquid hydrocarbon phase with the CPA and SRK/HV EoS, for the quaternary system MEG – water – methane – toluene.

Table 6.9. VLE prediction of the quaternary system MEG – water – methane - propane with the CPA and the SRK/HV EoS, expressed as % AAD. The binary parameters are presented in table 6.4 for the CPA EoS and in tables 6.1 and 6.2 for the SRK/HV. For the case of MEG – propane system no binary interaction parameter is used. Experimental data are taken from Ng and Chen[16].

				Liquid phase % AAD		**Vapor phase % AAD**	
compound	**Feed**	**T / K**	**P/bar**	**CPA**	**SRK/HV**	**CPA**	**SRK/HV**
MEG	16.7935	283	69	~0	0.1	-	-
Water	57.8455	283	69	~0	0.1	4.8	50.9
Methane	22.8244	283	69	20.3	20.1	~0	0.1
Propane	2.5366	283	69	56.5	128	0.2	0.5
MEG	14.9477	283	138	0.1	0.1	-	-
Water	51.4875	283	138	0.1	0.1	43.5	14.3
Methane	30.2076	283	138	24.9	25.1	~0	~0
Propane	3.3571	283	138	65.8	137	0.3	0.1
MEG	14.0019	283	210	0.1	0.1	-	-
Water	48.2296	283	210	0.1	0.1	29.8	74.7
Methane	33.9004	283	210	23.6	24.4	0.2	0.2
Propane	3.7781	283	210	54.3	122	1.9	2.0
MEG	17.305	310.9	69	~0	~0	41.4	6.1
Water	59.6071	310.9	69	0.1	0.1	43.1	79.1
Methane	20.7785	310.9	69	35.9	29.5	~0	~0
Propane	2.3093	310.9	69	109	157	0.5	0.7
MEG	14.1776	310.9	138	0.1	0.1	7.4	135
Water	48.8347	310.9	138	0.1	0.1	10.8	35.7
Methane	33.2883	310.9	138	41.3	33.2	0.1	0.1
Propane	3.6994	310.9	138	112	156	0.8	0.7
MEG	12.6544	310.9	210	0.1	0.1	1.2	263
Water	43.5882	310.9	210	0.1	0.1	11.9	53.6

Methane	39.3808	310.9	210	33.1	25.8	0.1	0.1
Propane	4.3766	310.9	210	94.1	134	0.7	0.8
		Average %AAD for all temperatures and pressures					
MEG				**0.1**	**0.1**	**16.6**	**135**
Water				**0.1**	**0.1**	**24.0**	**51.4**
Methane				**29.9**	**26.4**	**0.1**	**0.1**
Propane				**64.1**	**139**	**0.7**	**0.8**

Table 6.10. VLLE prediction of the quaternary system MEG – water – methane - toluene with the CPA and the SRK/HV EoS, expressed as % AAD. The binary parameters are presented in table 6.4 for the CPA EoS and in tables 6.1 and 6.2 for the SRK/HV. Experimental data are taken from Chen and Ng[17].

				Vapor phase % AAD		**liquid HC % AAD**		**aqueous phase % AAD**	
Compound	**Feed**	**T / K**	**P/bar**	**CPA**	**SRK/HV**	**CPA**	**SRK/HV**	**CPA**	**SRK/HV**
MEG	0.0549	275.4	69	-	-	14.8	80.0	~0	~0
Water	0.3512	275.4	69	41.4	17.3	25.3	53.6	~0	~0
Methane	0.3563	275.4	69	~0	~0	5.5	28.0	18.3	13.6
Toluene	0.2376	275.4	69	1.5	1.2	1.2	6.2	31.9	59.0
MEG	0.0596	323	69	-	-	17.5	11.3	0.1	0.1
Water	0.3819	323	69	20.3	4.9	15.8	21.4	~0	~0
Methane	0.3351	323	69	~0	~0	1.4	18.5	42.0	34.1
Toluene	0.2234	323	69	4.3	7.0	0.2	3.6	6.6	63.9
MEG	0.1379	323	69	-	-	16.2	14.4	~0	0.2
Water	0.2037	323	69	26.8	10.5	29.6	2.7	0.1	0.1
Methane	0.395	323	69	~0	0.1	5.7	13.2	23.1	10.2
Toluene	0.2634	323	69	3.0	5.7	1.1	2.7	3.8	53.5

	Average %AAD for all temperatures and pressures					
MEG	**-**	**-**	**16.2**	**35.2**	**~0**	**0.1**
Water	**29.4**	**7.9**	**23.6**	**25.9**	**~0**	**~0**
Methane	**~0**	**~0**	**4.2**	**19.9**	**27.8**	**19.3**
Toluene	**2.9**	**4.6**	**0.8**	**4.2**	**14.1**	**58.8**

Table 6.11. VLLE prediction of the 5 component system MEG – water – methane - propane – toluene with the CPA and the SRK/HV EoS, expressed as % AAD. The binary parameters are presented in table 6.4 for the CPA EoS and in tables 6.1 and 6.2 for the SRK/HV. For the binary system MEG – propane no binary parameters are used. Experimental data are taken from Ng and Chen[16].

				liquid HC % AAD		**aqueous phase % AAD**		**Vapor phase % AAD**	
	Feed	**T / K**	**P/bar**	**CPA**	**SRK/HV**	**CPA**	**SRK/HV**	**CPA**	**SRK/HV**
MEG	12.6217	283	69	26.2	66.5	~0	~0	73.7	47.7
Water	43.4755	283	69	23.2	56.9	0.1	0.1	56.7	38.5
Methane	21.7566	283	69	7.2	27.5	27.9	27.2	0.2	0.2
Propane	4.2302	283	69	0.8	4.2	28.9	85.3	3.0	4.7
Toluene	17.916	283	69	1.7	6.5	9.2	28.4	14.8	12.1
MEG	10.1406	283	138	12.6	35.9	0.1	~0	59.4	44.5
Water	34.9295	283	138	27.3	47.4	0.1	0.1	45.2	6.3
Methane	36.9347	283	138	15.0	36.7	32.5	32.5	0.5	0.5
Propane	3.4383	283	138	1.4	5.0	31.8	84.3	11.2	12.8
Toluene	14.5569	283	138	7.2	16.6	11.9	19.6	12.3	1.9
MEG	8.6839	283	205	0.3	10.8	0.1	0.1	65.9	80.3
Water	29.9117	283	205	23.2	52.8	0.1	0.1	43.9	37.7
Methane	47.4558	283	205	12.9	34.7	37.7	38.3	0.2	0.1
Propane	2.6993	283	205	9.3	0.4	13.4	56.7	2.4	3.4
Toluene	11.2494	283	205	10.0	24.1	23.7	0.6	6.3	12.7

MEG	12.6632	311	69	40.0	50.5	~0	~0	31.4	3.8
Water	43.6184	311	69	12.7	42.2	0.1	0.1	16.8	5.5
Methane	18.7729	311	69	9.8	30.4	41.2	32.5	0.6	0.6
Propane	4.7061	311	69	4.1	1.6	77.5	116	5.6	6.2
Toluene	20.2394	311	69	2.8	6.8	12.0	13.6	32.9	30.4
MEG	10.6092	311	138	34.1	31.9	0.1	~0	19.9	72.5
Water	36.5435	311	138	18.8	32.0	0.1	0.1	19.0	23.1
Methane	33.9229	311	138	7.9	27.7	43.0	34.4	0.4	0.3
Propane	3.5703	311	138	2.7	2.3	82.5	117	4.8	5.7
Toluene	15.3541	311	138	3.9	12.1	7.1	9.4	18.7	10.8
MEG	8.8627	311	205	24.0	12.1	0.1	0.1	43.4	58.4
Water	30.5277	311	205	16.8	33.9	0.2	0.2	22.2	37.7
Methane	44.9552	311	205	2.5	21.3	44.9	36.5	0.8	0.5
Propane	2.9535	311	205	10.2	2.9	29.2	51.4	7.1	7.7
Toluene	12.7009	311	205	3.0	16.0	21.4	25.6	22.3	9.8
		Average %AAD for all temperatures and pressures							
MEG				**22.9**	**34.6**	**0.1**	**~0**	**49.0**	**51.2**
Water				**20.3**	**44.2**	**0.1**	**0.1**	**34.0**	**24.8**
Methane				**9.2**	**29.7**	**37.9**	**33.6**	**0.5**	**0.4**
Propane				**4.8**	**2.7**	**43.9**	**85.1**	**5.7**	**6.8**
Toluene				**4.8**	**13.7**	**14.2**	**16.2**	**17.9**	**13.0**

Table 6.12. VLLE prediction of the 5 component system MEG – water – methane - propane – n-heptane with the CPA and the SRK/HV EoS, expressed as % AAD. The binary parameters are presented in table 6.4 for the CPA EoS and in tables 6.1 and 6.2 for the SRK/HV. For the binary system MEG – propane no binary parameters are used. Experimental data are taken from Ng and Chen[16].

				liquid HC % AAD		**aqueous phase % AAD**		**Vapor phase % AAD**	
Compound	**Feed**	**T / K**	**P/bar**	**CPA**	**SRK/HV**	**CPA**	**SRK/HV**	**CPA**	**SRK/HV**
Water	55.3263	283	69	50.9	51.5	~0	~0	57.2	39.4
MEG	16.0622	283	69	22.1	560	~0	~0	-	-
Methane	17.0152	283	69	0.4	13.2	20.1	19.9	0.2	0.2
Propane	2.1921	283	69	0.5	5.1	64.2	139	8.2	7.1
n-heptane	9.4043	283	69	0.1	6.0	40.6	1 order	0.8	3.7
Water	45.716	283	138	48.3	68.6	0.1	0.1	38.7	20.2
MEG	13.2721	283	138	24.1	573	0.1	0.1		
Methane	32.762	283	138	6.6	4.1	24.0	24.1	~0	0.1
Propane	1.5596	283	138	7.0	2.9	84.8	160	6.4	5.6
n-heptane	6.6903	283	138	8.9	5.8	52.3	1 order	9.8	2.5
Water	38.6904	283	205	61.6	26.1	0.1	0.1	59.2	10.8
MEG	11.2325	283	205	78.3	6.9	0.1	0.1	-	-
Methane	41.9985	283	205	6.2	4.8	26.5	27.0	2.7	1.4
Propane	1.5276	283	205	12.2	6.4	65.9	128	7.6	4.0
n-heptane	6.551	283	205	19.3	15.5	60.8	745	42.9	22.0
Water	53.7259	311	69	32.4	30.8	0.1	0.1	42.4	26.9
MEG	15.5976	311	69	21.5	207	0.1	~0	35.4	102
Methane	16.523	311	69	9.6	2.4	39.2	31.1	0.3	0.4
Propane	2.6754	311	69	3.0	0.6	228	305	11.0	10.9
n-heptane	11.4782	311	69	4.2	1.1	32.5	490	4.3	0.5
Water	49.4834	311	138	36.3	30.2	0.1	0.1	36.4	2.3
MEG	14.3659	311	138	18.1	204	0.1	0.1	60.4	250
Methane	26.1223	311	138	7.2	3.9	40.9	32.8	0.1	0.3

Propane	1.8951	311	138	2.9	4.7	240	307	0.8	0.5
n-heptane	8.1334	311	138	8.5	4.0	38.3	1 order	11.7	25.0
Water	40.4945	311	205	18.2	73.7	0.2	0.2	36.7	18.0
MEG	11.7562	311	205	5.6	130	0.1	0.1	45.2	80.6
Methane	39.1072	311	205	9.7	1.7	43.3	35.9	1.9	0.7
Propane	1.6341	311	205	10.3	4.6	99.8	133	4.9	2.1
n-heptane	7.008	311	205	26.5	4.5	22.4	510	33.1	12.5
		Average %AAD for all temperatures and pressures							
Water				**41.3**	**46.8**	**0.1**	**0.1**	**45.1**	**19.6**
MEG				**28.3**	**280**	**0.1**	**0.1**	**47.0**	**144**
Methane				**6.6**	**5.0**	**32.3**	**28.5**	**0.9**	**0.5**
Propane				**6.0**	**4.1**	**131**	**195**	**6.5**	**5.0**
n-heptane				**11.3**	**6.2**	**41.2**	**1 order**	**17.1**	**11**

1 order: the model overestimates the solubility by an order of magnitude.

6.4. Conclusions

In this work the performance of CPA was tested for multicomponent multiphase equilibria of systems containing MEG, water, and aliphatic or aromatic hydrocarbons. Several multicomponent systems, at various conditions were tested, based solely on common and temperature independent interaction parameters. The performance of CPA was found to be very satisfactory, as is the case for the individual binary systems, suggesting that the model is a reliable tool for phase equilibrium calculations at various temperature and pressure conditions when MEG is used as gas hydrate inhibitor.

In parallel, the performance of a conventional engineering EoS/G^E model was tested. The chosen model is the SRK EoS using the Huron and Vidal mixing rule and the modified NRTL model as an activity coefficient model, with three fitted parameters, as originally suggested by Huron and Vidal. For binary water – hydrocarbon systems (both aromatics and aliphatics), it is shown that three parameters cannot correlate satisfactorily both solubilities. The performance of SRK/HV is further tested to LLE of binary systems containing glycols and hydrocarbons. It was shown that over limited temperature ranges the performance of SRK/HV is satisfactory (similar to CPA), but over broad temperature ranges, the model correlates satisfactorily only the HC solubility in the polar phase, but fails to represent the temperature dependency of the glycol solubility in the HC phase. For multicomponent multiphase equilibria of systems containing MEG, the performance of SRK/HV is overall satisfactory, but systematically inferior to CPA in the predicted solubility of MEG and water in the hydrocarbon phase.

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Chapter 7.

Application of the Cubic-Plus-Association (CPA) Equation of State to Mixtures with Polar Chemicals

7.1. Introduction

The CPA has been mostly applied to mixtures of interest to oil & gas industries, and relatively less attention has been given to systems of relevance to the chemical industry. A first application appeared recently for organic acids[1]. However, being a model (equation of state) that accounts for several of the specific interactions present in mixtures of interest to chemical industry, there is, in principle, no restriction in employing CPA to polar/high pressure mixtures. In this work, CPA is applied to two classes of mixtures containing polar chemicals and for which high pressure data are available: acetone-containing systems and dimethyl ether- (DME) mixtures.

The way this chapter approaches the acetone containing systems is by assuming that acetone is a self-associating component. This approach is based on the idea to maintain the simplicity of the model, providing an alternative instead of adding a polar term to account explicitly for polar effects. Therefore not only systems of acetone – hydrocarbons, but also water – acetone system at various temperatures and pressures, the acetone – methanol system and water – acetone – methanol VLE are tested. The reason for doing this is to test the applicability of this rather simple approach to several systems containing acetone, both in the presence of hydrocarbons and water and even more associating compounds (i.e. water – acetone – methanol); hence this simplified approach has the merit stated above.

7.2. Acetone containing mixtures

Acetone is a polar compound. According to Vinogradov and Linnell[2], who divide substances into four categories, acetone belongs to the group II (molecules with acceptor groups only such as ketones, ethers, and esters). As discussed by Von Solms et al.[3], for compounds of comparable molecular weight, the boiling point increases from ethers, through esters and ketones, to the associating alcohols; the same observation can be done for the enthalpy of vaporization. This does not mean that ketones are associating components, but more polar than the other components mentioned previously, with a dipole moment of around 3 D, compared to around 2 D for esters, alcohols, and water and around 1 D for ethers.

Thus, for describing acetone and other ketones, in principle, an additional “polar” term is needed in models like CPA and SAFT that do not explicitly account for polar effects. However, it is tempting to consider simpler ways of resolving this problem. Moreover, although acetone is not a self – associating component, it strongly interacts (cross-associates or solvates) with water, which is responsible for the complete miscibility of this mixture in the whole temperature and pressure range that has been studied. Solvation can be incorporated in CPA even if one of the two compounds is inert using mCR-1, as already presented in chapter 4. However it can be shown that the characteristic azeotropic behavior of acetone – hydrocarbon systems cannot be represented by the CPA (SRK) EoS if acetone is considered inert, unless a large interaction parameter is used.

This is possibly due to the polar effects that are not accounted for explicitly by the CPA (SRK) equation of state (SAFT suffers also from the same limitation). An alternative way of resolving this problem is by assuming that acetone is a “self-associating compound” and thus estimate five parameters. A similar approach was followed by von Solms et al.[3] with the simplified PC-SAFT equation of state, testing however the validity of this approach for limited cases.

Table 7.1 provides two sets of pure component parameters for acetone, one when acetone is considered inert and one set when acetone is treated as an associating component using the 2B scheme. Figure 7.1 presents the experimental and predicted second virial coefficients for acetone using the two sets. Although the two sets are equivalent in the representation of vapor pressures and liquid densities, only the “associating” acetone can represent the second Virials satisfactorily.

Table 7.1. Pure component CPA parameters for acetone and DME.

Compound	a_0 **(bar l^2 mol^{-2})**	b **(l/mol)**	c_1	ε^{AB} **(bar l mol^{-1})**	β^{AB} ***10^3**	T_c **(K)**	**ΔP** (%)	**Δρ** (%)
DME	0.0496	8.4354	0.72125	-	-	400.1	0.3	0.8
Acetone inert	0.0619	13.996	0.80023	-	-	508.2	0.4	0.6
Acetone 2B	0.0592	7.8643	0.99510	111.73	289	508.2	0.3	0.2

Figure 7.2 shows a typical plot for an acetone – hydrocarbon system, treating acetone either as inert or as self-associating. When treating acetone as an inert component, the CPA EoS (actually SRK in this case) fails to represent the physical picture of the system, i.e. the azeotropic behavior, when no interaction parameter (k_{12}=0.0) is used. An adequate correlation of the system requires a rather high value of interaction parameter, much higher compared to the k_{12} used e.g. for alcohol-

alkanes. On the other hand, assuming that acetone is self-associating, a very satisfactory prediction of the VLE is achieved. Similar results are obtained for other acetone-alkane mixtures as can be seen in Table 7.2.

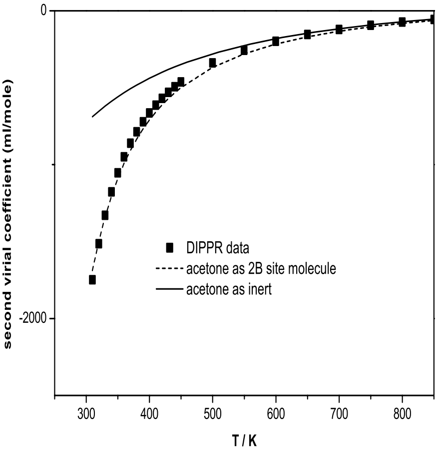

Figure 7.1. Experimental and predicted second virial coefficients for acetone using CPA and the two sets of parameters for acetone, “inert” and “2B” ones.

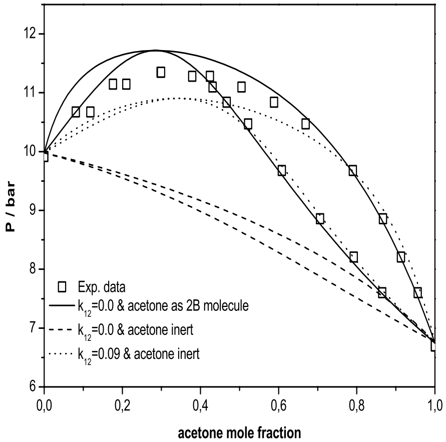

Figure 7.2. VLE prediction and correlation of acetone – pentane at 397.7K when acetone is considered as inert or self-associating compound. Exp. data from Campbell et al.[4].

VLE prediction/correlation results presented in recent publications[5-7] using the polar SAFT (or polar PC-SAFT) EoS are similar to the results obtained in this work treating acetone as self-associating. Adding a polar term may be a more rigorous approach since it is based on the physical picture of the molecule but it adds to the complexity of the model e.g. extra pure compound parameters that need to be determined from data and uncertainty of how the model can be used to both polar and associating compounds e.g. acetone-water mixtures.

Next, VLE of acetone-water has been considered. Von Solms et al.[3] presented VLE calculations of this system at 473.15K with simplified PC-SAFT treating acetone as a 2B associating compound and using k_{12}=0.0. The results were compared to the performance of the model when acetone is considered to be a non – self associating (inert) component. A successful performance of the model in indeed demonstrated. Similar predictive performance to PC-SAFT is obtained with CPA using

ECR and k_{12}=0.0, while the use of a binary interaction parameter would improve the results as demonstrated in figure 7.3. Table 7.3 provides results also at other temperatures using a common binary interaction parameter k_{12}=-0.14 with the CPA EoS. At the very low temperature of 298.15K where the polar forces are more pronounced a different binary interaction parameter was used, since the use of the aforementioned k_{12}=-0.14 would give an error in vapor pressure of 14%. The polar SAFT model has not been yet applied to the classical acetone – water system. When this is done, this will be a crucial test of the performance of both the Wertheim's and polar terms as compared to the simpler approach suggested here.

Table 7.2. VLE prediction and correlation results for acetone – hydrocarbon mixtures.

			2B for acetone			**acetone as inert**		
System	**Ref.**	**T**	k_{12}	**ΔP%**	**Δy*100**	k_{12}	**ΔP%**	**Δy*100**
acetone-hexane	8	293.15	0.0	5.6	3.0	0.0	20.7	9.8
			0.019	1.7	1.7	0.083	4.1	2.8
	9	308.15	0.0	5.2	2.8	0.0	20.7	8.4
			0.019	2.4	2.0	0.083	2.8	2.4
	9	318.15	0.0	4.8	2.8	0.0	20.2	8.4
			0.019	2.3	2.2	0.083	2.9	2.4
	9	328.15	0.0	3.6	2.6	0.0	18.8	8.4
			0.019	2.1	2.0	0.083	2.7	2.5
acetone-pentane	8	298.15	0.0	5.0	3.5	0.0	20.5	8.4
			0.026	3.0	1.7	0.085	4.6	2.7
	7	372.7	0.0	1.8	1.9	0.0	14.8	4.7
			0.0	1.8	1.9	0.085	2.9	1.2
	7	397.7	0.0	1.8	1.4	0.0	13.1	4.4
			0.0	1.8	1.4	0.085	2.6	1.2
acetone-butane	10	293.15	0.0	8.0	2.4	0.0	23.2	5.6
			0.035	3.5	0.8	0.088	5.5	0.9
	10	313.15	0.0	5.9	2.3	0.0	20.9	5.8
			0.035	2.9	1.0	0.088	5.0	0.9
acetone-cyclohexane	11	298.15	0.0	7.7	3.4	0.0	26.1	15.0
			0.022	5.7	2.9	0.1	5.9	4.5
	12	323.15	0.0	6.6	2.5	0.0	24.7	9.2
			0.022	2.4	1.6	0.1	2.2	2.0
Average (prediction)				**5.1**	**2.6**		**20.3**	**8.0**
Average (correlation)				**2.7**	**1.7**		**3.7**	**2.1**

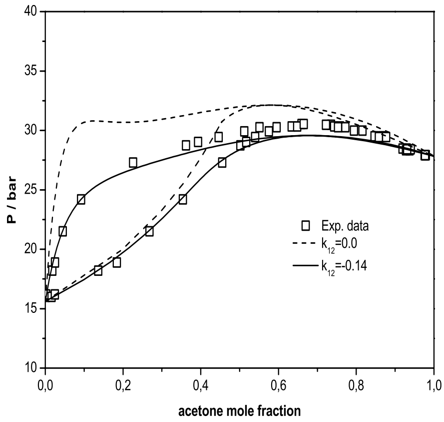

Figure 7.3. VLE prediction (k_{12}=0.0) and correlation for acetone – water at 473.15K with ECR and k_{12}=-0.14. Experimental data from Griswold et al.[13]

Table 7.3. VLE correlation results for acetone – water with CPA and ECR. In parenthesis are the results with SRK.

T (K)	Ref.	k_{12} with ECR	ΔP%	Δy*100
298.15	14	-0.171	6.6	2.0
		(-0.283)	(25)	(5.2)
323.15	15	-0.14	5.5	1.5
		(-0.254)	(17.6)	(3.5)
373.15	13	-0.14	2.6	1.4
		(-0.227)	(11.7)	(5.6)
423.15	13	-0.14	2.5	0.6
		(-0.190)	(8.6)	(3.5)
473.15	13	-0.14	2.1	0.7
		(-0.162)	(7.3)	(2.8)
523.15	13	-0.14	3.0	1.3
		(-0.126)	(6.8)	(3.7)
Average CPA			**3.7**	**1.3**
Average SRK			**12.8**	**4.1**

Successful modeling of acetone-water VLE has been presented by Dahl et al.[16] using the MHV2 model (SRK EoS with modified UNIFAC of Larsen et al. in the mixing rule). The authors focused on high-pressures, i.e. temperatures above 373.15K and the percentage deviations in pressure reported are 4.6% (373), 2.6% (473), 0.8% (523). The performance of CPA at these high temperatures is also improved compared to the lower temperatures (for example 298.15K), as can be seen from the results shown in Table 7.3. The performance of CPA is similar to that of MHV2.

Finally, the VLE of acetone(1) – methanol(2) – water(3) is considered based solely on binary interaction parameters. The binary interaction parameters used at both 373.15K and 523.15K are k_{12}= 0.031, k_{13}= -0.14 and k_{23}= -0.09 and ECR rule is used for all three cross-associating systems. Table 7.4 presents the results. The prediction of the VLE of the multicomponent system is very satisfactory, indicating that the correlations of the binary systems, even if it is not entirely optimum, can be considered overall adequate for the representation of multicomponent mixture.

Table 7.4. Prediction of high pressure VLE for the system acetone(1) – methanol(2) – water(3) using CPA and ECR. Experimental data from Griswold and Wong[13].

T (K)	NP	Δy (1)*100	Δy (2)*100	Δy (3)*100	ΔP (%)
373.15	51	2.7	2.7	1.7	2.6
523.15	57	0.6	1.5	1.4	1.2

7.3. Modeling of binary and ternary systems containing DME

This last application is concerned with multicomponent, multiphase (VLLE) equilibria of mixtures containing dimethyl ether (DME), water and gases (CO_2, nitrogen). Such data are of importance to the manufacturing of DME and recent experimental data have been reported[17]. Rigorously speaking, DME is a non – associating component although solvation is possible with polar compounds e.g. water. The CPA parameters estimated from vapor pressures and liquid densities are shown in Table 7.1. Excellent correlation of DME-CO_2 is achieved at all temperatures, as shown for a typical case in figure 7.4.

VLE of water – DME can be best described if, as physically expected, DME is allowed to solvate with water. This becomes evident as description of DME-water VLE without accounting for solvation is possible at the cost of a rather large negative interaction parameter (k_{12}=-0.313 at 323.15 K). Solvation is implemented in a way previously presented for aqueous/polar mixtures with aromatic hydrocarbons using the mCR-1 combining rule. Figure 7.5 presents VLE correlation results using this approach. The performance of the model is satisfactory and the results are improved compared to when only a binary interaction parameter k_{12} is used.

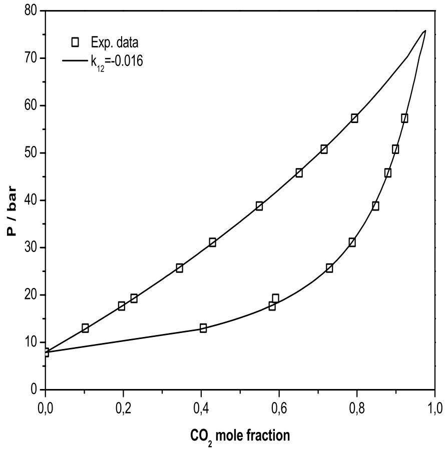

Figure 7.4. VLE correlation of DME – CO_2 at 308.65K. Experimental data from Laursen et al.[17].

Equally good results are obtained at higher temperatures using the same value of the cross association volume BETCR and fitting only the k_{12} parameter. The k_{12}'s are, as could be anticipated, a bit smaller at higher temperatures, namely -0.13 at 348.15 K and -0.124 at 373.15 K. Finally, for the binary system of CO_2 – water a value of k_{12}= -0.066 was used, which was optimized from VLE data[19] within the range 298.28 – 318.15K, providing excellent correlation results at all temperatures.

CPA has been then applied to VLLE of the ternary system of DME – CO_2 – water for which recent data[17] are available at three temperatures (298, 308 and 318 K). The feed composition is not reported for exact flash calculations. However, it is found that in the three phase region (vapor – liquid – liquid) a change in the feed composition results in a very minor change in the equilibrium composition. Sample results are shown in figures 7.6-7.8 for one of the three temperatures (similar results are obtained at the other temperatures as well using the same values of the binary interaction parameters). Results are presented as concentrations at the various pressures of the three components in the vapor and the two liquid phases. Table 7.5 presents an overview of the performance of the model at the various conditions.

The performance of CPA is overall satisfactory for the prediction of the multicomponent system, based solely on a single interaction parameter for the systems DME – CO_2 and water – CO_2 respectively. Two parameters are used for water – DME, since DME is considered as non self-associating component but capable of solvating with water. As table 7.5 illustrates, the prediction of the gas phase is very adequate for the light components (which are however present in high amounts), while for the calculated gas phase water content CPA gives errors of the order of the experimental one (reported[17] to be 25%). Larsen reports[17] that the measured values were found to deviate within 50% for measurements on the detection limit of the GC, without however reporting if this was the case for the water content in the upper liquid phase and for DME in the aqueous (lower liquid) phase. If this is the case, then the predicted values of CPA are within the experimental uncertainty.

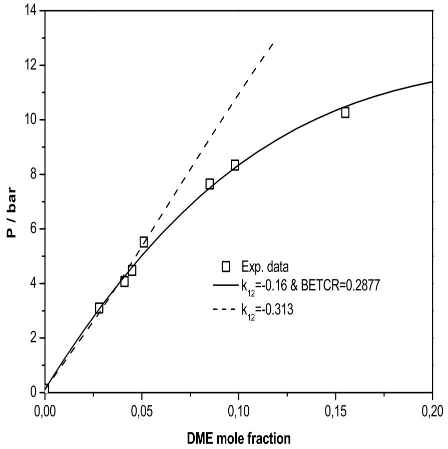

Figure 7.5. VLE correlation of DME – water at 323.15K using an interaction parameter k_{12}=-0.16 and BETCR=0.2877. For comparison the results without accounting for association are presented (k_{12}=-0.313). Exp. data are taken from DozodeFernandez et al.[18]

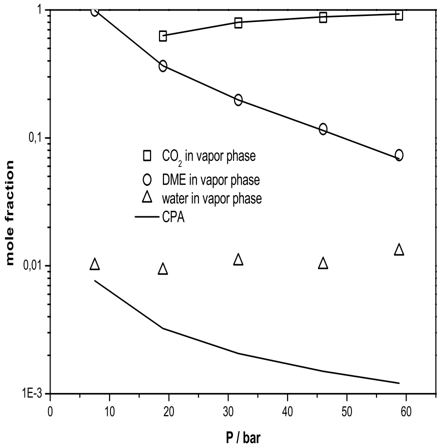

Figure 7.6. VLLE predictions for the ternary system water (1) –DME (2) –CO_2 (3) at 308.15K. The interaction parameters used are k_{12} = -0.16 and BETCR=0.2877, k_{13} = -0.066 and k_{23} = -0.016. Experimental data are taken from Laursen et al.[17].

Then the nitrogen-water-DME system was considered. The correlation of VLE of N_2 – DME[17] is very satisfactory at all temperatures considered (298, 308, 318), using k_{12}=0 (prediction), as shown in figure 7.9. The VLE of the binary system of H_2O – N_2 is of some interest. Extensive experimental data are available[20] at various temperatures. Figures 7.10 and 7.11 present the correlative and predictive performance of CPA at 310.93 K. The interaction parameter seems to have little importance in the case of the solubility of water in the vapor phase, but seems to have a large influence in the case of the solubility of nitrogen in water.

The large negative k_{12} could be due to solvation phenomena (since N_2 is a weak quadrupole there is possibility for some solvation with water) or the sensitivity of the calculations as the solubilities in the aqueous phase are very low. It is of particular interest that at higher temperatures (366.48 and 477.6 K) both solubilities (in the liquid and vapor phase) could be represented with k_{12}=0.0.

Figures 7.12- 7.14 show the prediction of the VLLE of the ternary system with CPA at 308.15K. These calculations are based on k_{12}=0 for water-nitrogen but very similar results are also obtained when k_{12}=-0.2 is used for this binary. For N_2 – DME no binary interaction parameter is used (k_{12}=0) while for water – DME two interaction parameters are used, due to the solvation (k_{12} = -0.16 and BETCR=0.2877). The same parameters were also used in the case of the ternary system water – DME – CO_2. Table 7.5 summarizes the results.

The prediction of the VLLE of this ternary system is not satisfactory. Only the prediction of the lower liquid phase, which contains mainly water, is relatively satisfactory for the components that are present in considerable amounts. The prediction of the upper liquid phase for the components that are present in significant amounts is in serious error and the same is valid for the gas phase. No satisfactory explanation for this discrepancy was found. More specifically:

i) Similar multicomponent results are obtained using either k_{12}=0.0 or -0.2 for the water-nitrogen system

ii) The water-DME system has been revisited by assigning association sites to DME, but similar results are obtained, thus there is no reason for resulting in more complex approaches.

iii) Several feed compositions were tested, but the change is the equilibrium solubilities is negligible.

The performance of CPA for these ternary mixtures is similar to the SRK/modified Huron-Vidal (MHV1) model employed by Laursen for modeling these systems[21]. Laursen used the NRTL model in the mixing rule with two interaction parameters fitted to binary data (the non-randomness parameter was fixed to $\alpha_{12} = 0.2$). Thus, even when such local composition model is employed (as mixing rule) with two parameters, no improved representation is obtained for the nitrogen-containing multicomponent mixture.

Table 7.5. VLLE prediction results for the ternary systems of CO_2 (1) – DME (2) – water (3) and N_2 (1) – DME (2) – water (3) with the CPA EoS, expressed as %AAD of mole fraction (x for the liquid phase or y for the vapour) of the compound i in each phase.

		% AAD in lower liquid			**% AAD in upper liquid**			**% AAD in vapor phase**		
System	**T / K**	**x_1**	**x_2**	**x_3**	**x_1**	**x_2**	**x_3**	**y_1**	**y_2**	**y_3**
CO_2 (1) –DME (2)- H_2O (3)	298.15	25.0	34.2	1.5	7.2	11.4	59.8	2.5	7.8	35.2
	308.15	15.4	41.0	1.8	2.1	6.6	65.2	1.2	2.3	69.1
	318.15	21.2	80.1	2.7	3.6	4.4	57.3	1.5	6.6	52.5
N_2 (1) –DME (2)- H_2O (3)	298.15	54.0	5.7	1.0	219.4	5.9	63.1	20.7	40.7	79.0
	308.15	132	6.4	1.1	233.3	8.2	60.5	30.2	38.7	66.2
	318.15	119	18.7	2.8	213.7	5.6	51.5	35.3	38.1	42.0

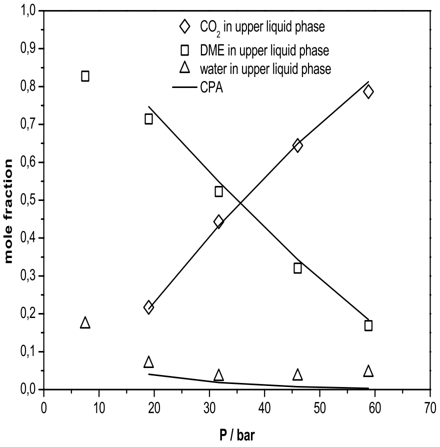

Figure 7.7. VLLE predictions of the upper liquid phase for the system water(1)–DME(2)–CO_2(3) at 308.15K, with parameters as in figure 11.

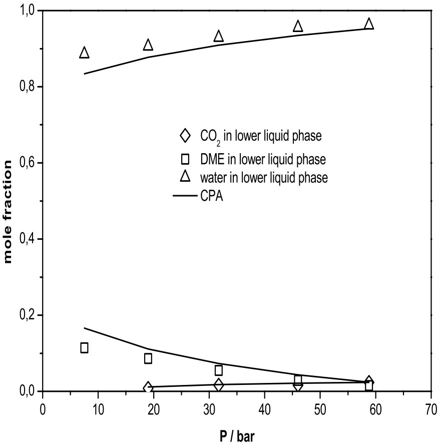

Figure 7.8. VLLE predictions of the lower liquid phase for the system water(1)–DME(2)–CO_2(3) at 308.15K, with parameters as in figure 11.

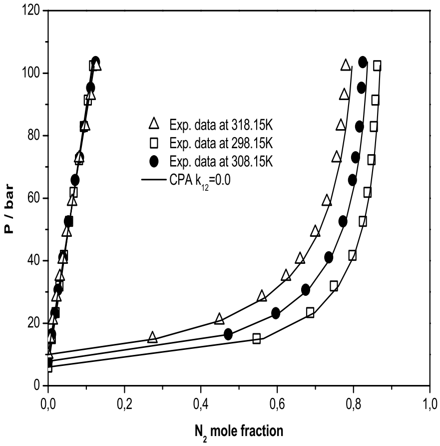

Figure 7.9. VLE of N_2 – DME system at various temperatures with k_{12} = 0.0. Exp. data from Laursen et al.[17].

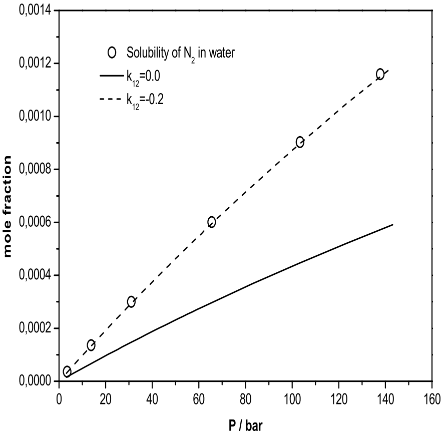

Figure 7.10. Prediction and correlation of the solubility of N_2 in water at 310.93K with CPA. Exp. data from Gillespie et al.[20]

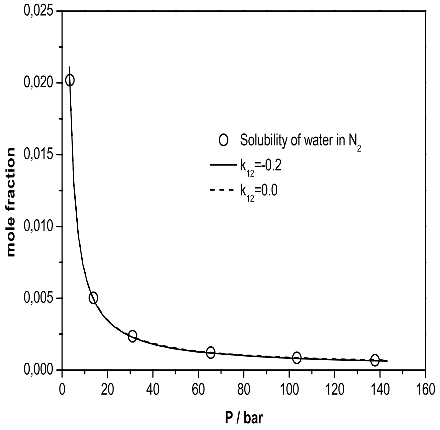

Figure 7.11. Prediction and correlation of the solubility of water in N_2 at 310.93K with the CPA EoS. Experimental data from Gillespie et al.[20]

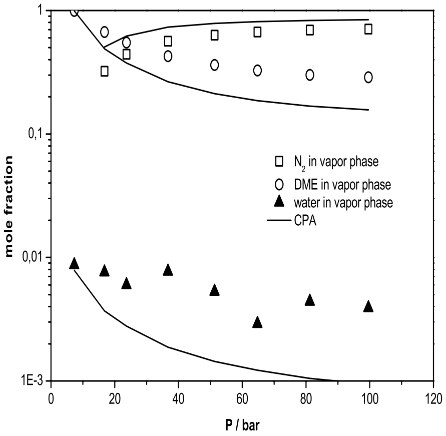

Figure 7.12. VLLE predictions for the ternary system water (1) –DME (2) –N_2 (3) at 308.15K. Experimental data from Laursen et al.[17].

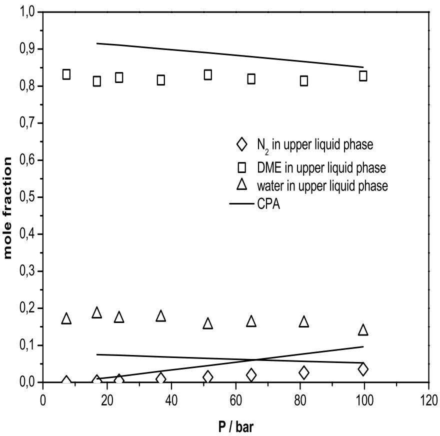

Figure 7.13. VLLE predictions for the ternary system water (1) – DME (2) –N_2 (3) at 308.15K.

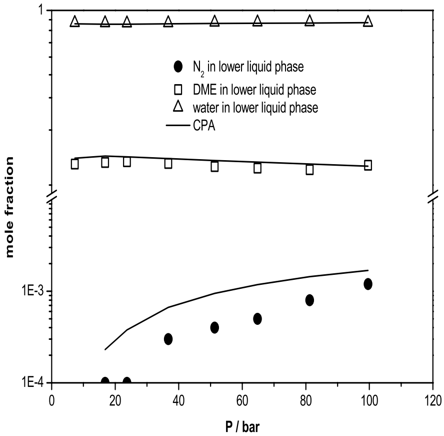

Figure 7.14. VLLE predictions for the ternary system water (1) – DME (2) –N_2 (3) at 308.15K.

7.4. Conclusions

The CPA equation of state has been applied to phase equilibria of complex polar and associating compounds. Emphasis has been given on multicomponent, multiphase equilibria and high pressures. More specifically, two cases have been considered: (i) acetone-hydrocarbons and acetone-water high pressure VLE, and (ii) VLLE of dimethyl ether mixtures with water and gases (CO_2, nitrogen). The mixtures considered in this work are of interest to applications especially in the chemical industry. The basic conclusions of this work are:

(i) Satisfactory VLE calculation of acetone-hydrocarbons is achieved if acetone is allowed to self-associate. This is a practical way to describe the non-ideality of such mixtures, otherwise explicit account of the polarity is required.

(iii) The correlation of high-pressure acetone-water VLE is also satisfactory, although the interaction parameters remain high, despite explicitly accounting for association/solvation effects. Excellent prediction is obtained for water-methanol-acetone VLE.

(iv) Ethers are, like ketones, polar compounds and it is important to account for solvation in dimethyl-ether water systems.

(v) Satisfactory VLLE predictions are obtained for CO_2-water-DME, but less satisfactory for nitrogen-water-DME. Results with conventional local-composition models using two parameters per binary (MHV1/NRTL) are similar to those of CPA for both systems and it is unclear why in particular the nitrogen-containing system provides inferior results.

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Chapter 8.

Prediction of Water Content of High Pressure Nitrogen, Methane and Natural Gas

8.1. Introduction

The water content of natural gas creates problems during transportation and processing, the most severe of which is the formation of gas hydrates. A major consequence of their nuisance behavior is that they could block pipelines, such as transmissions lines transporting water and condensed hydrocarbons. Pipeline conditions are usually in the temperature range of 50 to -20 ^{o}C and a pressure range 50-250 bar, although it is occasionally of interest to predict water content at both higher and lower temperatures. Accurate description of the equilibrium water content of natural gas is therefore of great importance to natural gas processors. However, there are large variations between experimental data, while the usual cubic equations of state do not give accurate description of water behavior.

In this chapter we want to test if CPA can be used to predict (i.e. no binary interaction parameter used) the gas phase water content of natural gas components and mixtures in equilibrium with liquid water, ice or hydrate. Initially, nitrogen and methane have been singled out as pure components. Nitrogen because it only forms hydrates at very low temperatures in the actual pressure ranges; methane because it is the dominant component in natural gas and also forms hydrates at high temperatures (e.g. at 25 ^{o}C). To compute the hydrate equilibria, a thermodynamically consistent description is chosen, by using the same equation of state for describing both the liquid and the vapour phase. The critical properties and the acentric factor are used for all inert components with CPA calculations, while the CPA parameters for water are presented in chapter 1.

The performance of the CPA EoS is, finally, compared to GERG-water[1] model, which is the ISO standard model for calculations of natural gas water content, suggested by the European gas research group GERG. The description of GERG-water model is presented in Chapter 1. Being an equation of state, GERG – water model could be also combined with the modeling approach presented in section 8.2. However, this is EoS specifically for water in natural gas limited to temperatures below 313 K while the binary interaction parameter (k_{12}) of the model is explicitly fitted to selected binary data including also equilibrium data between hydrate – vapor or ice – vapor. Hence, the solid phase is treated as a "pseudo" liquid phase; a two phase PT-flash calculation is only required for gas phase water content calculations over the suggested temperature and pressure range. Therefore, the GERG-water model is not combined with a hydrate or ice phase-model, as is the case with CPA, but used as suggested by GERG[1].

8.2. Thermodynamic Modeling

When computing hydrate equilibria, the values of fugacities of all the components present in the mixture at the different phases need to be calculated. The different phases that are considered for the applications in this chapter are the following: vapor (V), aqueous liquid phase (L_W), liquid hydrocarbon phase (L_H), hydrate structure I (H_I), hydrate structure II (H_{II}), and Ice (I).
Starting from the iso-fugacity criteria:

$$f_i^H = f_i^\alpha \tag{8.1}$$

Where α denotes vapor (V), aqueous liquid phase (L_W), liquid hydrocarbon phase (L_H) or Ice (I) phase and H is the hydrate phase. The fugacity f_i^a of the component i in the vapor or liquid phase is obtained from the CPA EoS, according to the following equation:

$$f_i^a = x_i \varphi_i^a P \tag{8.2}$$

Where P is the total pressure of the system while x_i is the mole fraction of the component i in the vapor or liquid phase, respectively.

8.2.1. Fugacity of ice

The water fugacity in the ice phase at the desired pressure of the system P is given by the following equation:

$$\ln f_w^{ICE} = \ln f_{w,P\_ref}^{ICE} + \frac{1}{RT} \int_{P\_ref}^{P} V_W^{ICE} dP \tag{8.3}$$

Where f_{w,P_ref}^{ICE} is the fugacity of water in the ice phase at the reference pressure P_ref (which is atmospheric pressure) while V_W^{ice} in the Poynting term correction, is the molar volume of ice which is obtained by the correlation suggested by Avlonitis[2]. The fugacity of water in the ice phase f_{w,P_ref}^{ICE} can be computed via such a difference term involving the heat of fusion ΔH^{fus} and the difference of heat capacity ΔC_p^{fus} between solid and liquid[3], similar to way the fugacity of the solid phase is calculated in the case of SLE:

$$\ln(f_{w,P\_ref}^{ICE}) = \ln(f_w^{L_0}) + \frac{\Delta H^{fus}}{RT_m}\left(1-\frac{T_m}{T}\right) + \frac{\Delta C_p^{fus}}{R}\left(\frac{T_m}{T}-1-\ln\left(\frac{T_m}{T}\right)\right) \tag{8.4}$$

The value of the melting temperature for water used in equation (8.4) is T_m=273.15K, the value of the heat of fusion at the melting temperature is ΔH^{fus}=6010 J.mol^{-1} while the difference in the heat capacity between the liquid and solid phase is ΔC_p^{fus}=37.29 J/mol*K.

8.2.2. Fugacity and Chemical potential of the hydrate phase

The fugacity of water in the hydrate phase is estimated according to the following equation[4]:

$$f_w^H = f_w^{EH} \exp\left(\frac{\mu_w^H - \mu_w^{EH}}{RT}\right) \tag{8.5}$$

In equation (8.5) f_w^{EH} is the fugacity of water in the hypothetical empty hydrate phase.

The chemical potential of the hydrate phase in equation (8.5) is obtained from the statistical model proposed by Van der Waals and Platteeuw[5]. The yielding expression for the chemical potential of the hydrate μ_W^H is:

$$\mu_W^H = \mu_W^{EH} + RT\sum_i \nu_i \ln\left(1-\sum_{\text{guests}\,m}\Theta_{mi}\right) \tag{8.6}$$

Where R is the universal gas constant, ν_i is the number of type i cavities per water molecule (which are: $\nu_1 = 1/23$ and $\nu_2 = 3/23$ for structure I hydrate and $\nu_1 = 2/17$ and $\nu_2 = 1/17$ for type II hydrates) and the summation is over all cavity types (both 1 and 2). Finally, the occupancy of cavity m by a component i, Θ_{mi}, is calculated as follow:

$$\Theta_{mi} = \frac{C_{mi} f_m}{1+\sum_{\text{guests}\,k} C_{ki} f_k} \tag{8.7}$$

Here f_k is the fugacity of a component k in the equilibrium phase obtained from an equation of state (CPA in this work) according to equation (8.2), the summation is over all hydrate-forming components while C_{mi} are the Langmuir constants. Two approaches exist concerning the computation of the Langmuir constants. The simplified approach, suggested by Parrish and Prausnitz[6], enables the use of the empirical equation:

$$C_{mi}(T) = \frac{A_{mi}}{T} \exp\left(\frac{B_{mi}}{T}\right) \tag{8.8}$$

Where A_{mi} and B_{mi} are fitted parameters. The more rigorous approach is to introduce a model potential experienced by the guest molecule in the cage, based on water-guest interactions. The Kihara potential is commonly used; Parrish and Prausnitz[6] suggest that both approaches yield very similar results within the temperature range 260–300K. In this work the former and computationally cheaper approach is used over the whole T range, as also followed by Munck et al.[7]. The parameters A_{mi} and B_{mi} are fitted to experimental three – phase equilibrium data. As shown by Munck et al.[7] the simultaneous fitting of those parameters to simple hydrate data and mixtures containing more guess molecules, provide parameters which can be satisfactorily used for predictions of multicomponent mixtures.

The fugacity of water in the hypothetical empty hydrate phase is described in this work assuming that the hypothetical empty hydrate phase behaves as a solid phase. Hence, the fugacity of water in the hypothetical empty hydrate solid phase is described by the equation:

$$f_W^{EH} = P_w^{EH} \phi_w^{EH} \exp \int_{P_w^{EH}}^{P} \frac{V_w^{EH}}{RT} dP \tag{8.9}$$

The fugacity coefficient ϕ_w^{EH} of water vapour over the empty hydrate phase is set to unity as is typically the case for any pure solid phase (i.e. ice). The vapor pressure of the hypothetical empty hydrate structures I and II, P_w^{EH} (in atm), is calculated based on the empirical equations proposed by Sloan[4]:

$$\ln P_w^{EH} = 17.440 - 6003.9/T \text{, for structure I} \tag{8.10}$$

$$\ln P_w^{EH} = 17.332 - 6017.6/T \text{, for structure II} \tag{8.11}$$

Sloan[4] obtained those expressions by equating the fugacity of ice to the fugacity of water in the hydrate phase given by equation (8.5) for a number of different components over the three phase ice – hydrate – vapour (IHV) line. In this way the concept of a universal empty hydrate vapour pressure for each structure (sI or sII) was introduced, since the values of $\ln P_w^{MT}$ were found to be linear when plotted over 1/T. A similar concept was recently followed by Klauda and Sandler[8,9], who fitted however the vapor pressure of the empty hydrate lattice for each guest molecule. It is of interest to mention that Ng and Robinson[10], following a similar procedure, suggested the concept of a universal fugacity expression for each hydrate structure and performed satisfactorily vapor – hydrate equilibrium calculations in the absence of a liquid phase.

In order to obtain the equations (8.10) and (8.11) the difference in the exponential term of equation (8.5) has to be calculated beforehand; therefore the fugacity f_k of the component k in the vapor phase (see equation 8.7) and Langmuir constants (expressed either by equation 8.8 or using Kihara potential) should be calculated beforehand as well, typically using existing parameters for the Langmuir constants, which are obtained from the conventional approach of modeling the hydrate phase. The conventional way to obtain the fugacity of the hypothetical empty hydrate lattice is by considering the difference in the chemical potential of water in the empty hydrate lattice and that of pure ice or pure liquid water:

$$f_w^{EH} = f_w^{ICE/L_0} \exp\left(\frac{\Delta\mu_w^{EH-ICE/L_0}}{RT} \right) \tag{8.12}$$

$$\begin{aligned} \frac{\Delta\mu_w^{EH-ICE}}{RT} &= \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T} \frac{\Delta h_w^{EH-ICE}}{RT^2} dT + \frac{\Delta V_w^{EH-ICE} P}{RT} \\ \frac{\Delta\mu_w^{EH-L_0}}{RT} &= \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T} \frac{\Delta h_w^{EH-ICE} + \Delta h_w^{ICE-L_0}}{RT^2} dT + \frac{\Delta V_w^{EH-ICE} P + \Delta V_w^{ICE-L_0} P}{RT} \end{aligned} \tag{8.13}$$

Equation (8.12) is a function of $f_w^{L_0}$ (i.e. the fugacity of pure liquid water since if ice is the stable phase equation 8.3 is used) obtained at the desired T and P from an EoS. Li and Englezos[11] recently used SAFT EoS for hydrate calculations based on the conventional approach without however reporting if they obtained the fugacity of ice in relation to the hypothetical pure liquid water from equation (8.3). $\Delta\mu_w^0$ is the chemical potential difference between the empty hydrate and ice at the reference condition of $T_0 = 273.15$ K and zero pressure, while Δh_w^{EH-ICE} and ΔV_w^{EH-ICE} are the enthalpy and volume differences between the empty hydrate lattice and ice, respectively. Finally $\Delta h_w^{ICE-L_0}$ is usually expressed by the following equation:

$$\Delta h_w^{ICE-L_0} = \Delta h_w^{fus} + \int_{T_0}^{T} \left[\Delta C p_w^0 + b(T - T_0) \right] dT \tag{8.14}$$

This method is predicated on the values of $\Delta\mu_w^0$, Δh_w^{EH-ICE} and ΔV_w^{EH-ICE} used. Depending on these values and the calculated $f_w^{L_0}$ with the EoS used, Langmuir constants would have to be optimized for reliable predictions of hydrate formation conditions.

We further show that the use of CPA for estimating the fugacity f_k of a component k in the equilibrium vapor phase, the different way for estimating Langmuir constants and the assumption that equation (8.9) is valid over the whole temperature and pressure range (and not limited over the IHV region) does not influence the overall performance of the hydrate model. This is because the calculated fugacity of water in the hypothetical empty hydrate phase (f_w^{EH}), when assuming the validity of equation (8.9), is similar to the empty hydrate fugacity obtained from equations (8.12) – (8.14) and CPA for calculating the $f_w^{L_0}$.

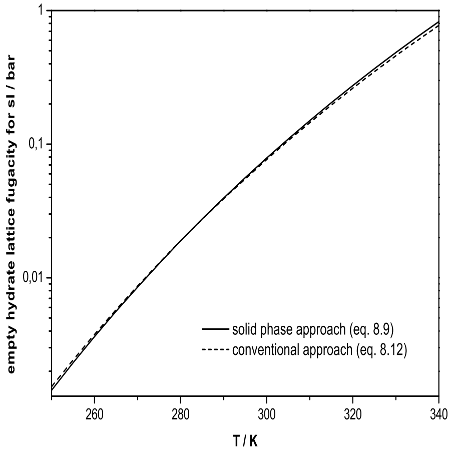


Figure 8.1. Comparisons of calculated fugacities of the hypothetical empty hydrate lattice for sI hydrate at 20bar using equation (8.9) or equation (8.12)

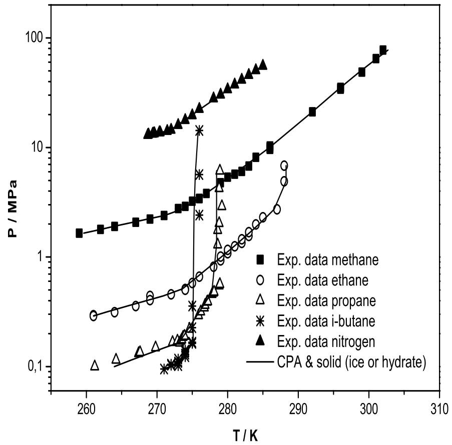


Figure 8.2. Comparisons of experimental and calculated dissociation temperatures of methane, ethane, propane, iso-butane and nitrogen.

The small differences will be anyhow taken into account when fitting the Langmuir parameters A_{mi} and B_{mi} from equation (8.8) to experimental three – phase equilibrium data. Figure 8.1 presents calculated fugacities of the hypothetical empty hydrate lattice for sI at 20bar, either using equation

(8.9) or equation (8.12). For equation (8.9) the molar volumes of the empty hydrates (I and II) are obtained from the correlations proposed by Avlonitis[2]. For equation (8.12) $f_w^{L_0}$ is directly obtained from CPA EoS, while $\Delta\mu_w^0$=1263 J/mol, Δh_w^{EH-ICE}=1389 J/mol, while in the liquid phase region 6011 J/mol is subtracted (i.e. equation 8.14 since the heat of fusion is required). In equation (8.14) the values used are ΔCp_w^0=-38.12 and *b*=0.141 for $T>T_0$, while for $T<T_0$ the values of ΔCp_w^0 and *b* are equal to zero. Finally ΔV_w^{EH-ICE}=3 ml/mol and $\Delta V_w^{ICE-L_0}$=1.6 ml/mol. Similar to the results presented in figure 8.1 is the performance of the calculated empty hydrate fugacities both at higher and lower pressures for both structures.

Table 8.1 presents the suggested parameters A_{mi} and B_{mi} for the Langmuir constants used with CPA. Four parameters are needed for compounds which can enter both small and large cavities. Only two parameters are needed for compounds which can only enter large cavities. The data used for simultaneous fitting of those parameters are tabulated in table 8.2. Figure 8.2 presents typical comparisons of experimental and calculated dissociation pressure of several simple hydrate systems with one guess molecule. For obtaining the values of A_{mi} and B_{mi} presented is table 8.1 the following procedure was followed: Methane and ethane parameters for structure I hydrates were obtained by simultaneously regressing equilibrium data for methane/water, ethane/water and methane/ethane/water data. All those mixtures form sI hydrates. Parameters for propane were obtained based only on the experimental data of propane/water mixture presented in table 8.2. The same methodology was followed for obtaining parameters for i-butane. Since both those components fit only in large cavities and thus two parameters can be optimized per component, considering only single gas data is an efficient way to obtain parameters which best fit the dissociation data. The parameters of propane and i-butane were further used to obtain sII parameters for methane while the sII parameters for ethane were obtained using the mixture data of ethane/propane/water presented in table 8.2. Similarly the sII parameters for nitrogen were obtained using nitrogen/water and nitrogen/propane/water data, while the sI parameters for nitrogen were obtained using nitrogen/methane/water data. One of the components, n-butane only forms sII hydrates in mixtures and thus the parameters were obtained using data for methane/n-butane/water mixture and using the previously obtained sII parameters for methane.

Table 8.1. Optimized values of A_{mi} and B_{mi} for calculating the Langmuir constants from equation (8.8).

		Small cavity		**Large cavity**	
Component	**Structure**	A_{mi} x10^3 **(K bar^{-1})**	B_{mi} **(K)**	A_{mi} x10^3 **(K bar^{-1})**	B_{mi} **(K)**
methane	I	0.621	2760	421.2	1963
	II	4.05	2637	295.2	900
ethane	I	0.0	0.0	109.8	2855
	II	0.0	0.0	89.4	3363
propane	II	0.0	0.0	79.9	3886
iso-butane	II	0.0	0.0	81.6	4000
n-butane	II	0.0	0.0	1053	2691
nitrogen	I	11.64	2159	400.1	1037
	II	7.18	2091	300	1150

The chosen EoS used for the calculation of the fugacity coefficients influences the overall calculations of hydrate formation conditions, when the same parameters in the Langmuir expression are used. For example Lundgaard and Mollerup[12] compared SRK, PR and a modified BWR EoS and showed that the difference in the calculated fugacity coefficients influence the calculated dissociation pressure for single water – gas systems, when using a single set of Kihara parameters for all models, obtained over the ice – vapor – hydrate line (because the influence of the gas phase fugacities is negligible). However an improvement in the calculations was presented[12] when fitting the Langmuir constants using all experimental data and not only data alone the ice – vapor – hydrate line. The results are similarly influenced when using different expression for the empty hydrate fugacity and same Langmuir constants parameters. A typical case is presented in figure 8.3, which presents calculated dissociation temperatures for methane hydrate. The solid line is when using the solid phase approach for obtaining the empty hydrate fugacity (equation 8.9) with Langmuir parameters (C_{mi}) obtained from equation (8.8) and parameters as presented in table 8.1. The dot line is when using the solid phase approach for obtaining the empty hydrate fugacity (equation 8.9) with Langmuir parameters (C_{mi}) obtained from the expression:

$$C_{mi}(T) = \frac{4\pi}{kT}\int_{0}^{R_i-\alpha_i} \exp\left(-\frac{W(r)}{kT}\right) r^2 dr \tag{8.15}$$

Where k is the Boltzman constant, R_i is the radius of cage i, α_i is the guess core radius and *W(r)* is the potential function: The Kihara potential function, as suggested by Mckoy and Sinanoglu[13], is used:

$$W(r) = 2z\varepsilon\left[\frac{\sigma^{12}}{R^{11}r}\left(\delta^{10}+\frac{\alpha}{R}\delta^{11}\right)-\frac{\sigma^{6}}{R^{5}r}\left(\delta^{4}+\frac{\alpha}{R}\delta^{5}\right)\right] \tag{8.16}$$

$$\text{Where } \delta^{N} = \frac{1}{N}\left[\left(1-\frac{r}{R}-\frac{\alpha}{R}\right)^{-N}-\left(1+\frac{r}{R}-\frac{\alpha}{R}\right)^{-N}\right] \tag{8.17}$$

The Kihara parameters for methane in equation (8.16) are taken from Sloan[4]: $\varepsilon / k = 154.54$K, $\sigma = 3.1615$Å and $\alpha = 0.3834$ Å.

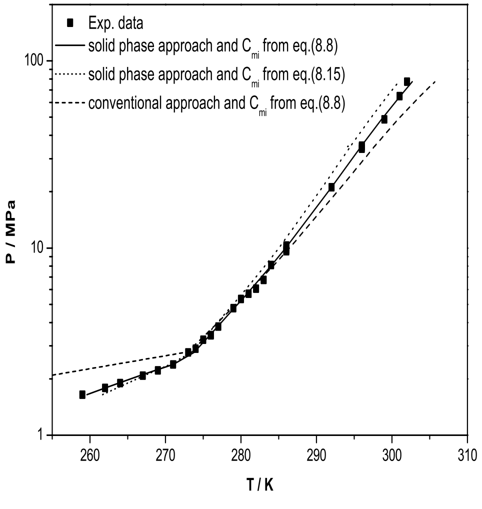


Figure 8.3. Comparisons of experimental and calculated dissociation temperatures of methane hydrate.

Table 8.2. Database used for regression of parameters A_{mi} and B_{mi}. The complete references are cited in the monograph of Sloan[4]. The vapor – hydrate – ice data for nitrogen are obtained from Van Cleeff and Diepen[36] since they are not included in the monograph of Sloan[4].

Parameters estimated	**Structure**	**Gas**	**Reference**
CH_4 : 4 parameters	*Structure I*	CH_4	*Roberts et al. (1940)*
			Deaton and Frost (1946)
			Marshall et al. (1964)
			Kobayashi and Katz (1949)
			McLeod and Campbell (1961)
		$CH_4 + C_2H_6$	*Deaton and Frost (1946)*
			McLeod and Campbell (1961)
			Holder and Grigoriou (1980)
CH_4 : 4 parameters	*Structure II*	$CH_4 + C_3H_8$	*Deaton and Frost (1946)*
			McLeod and Campbell (1961)
		CH_4 + i-C_4H_{10}	*Ng and Robinson (1976)*
C_2H_6 : 2 parameters	*Structure I*	C_2H_6	*Roberts et al. (1940)*
			Deaton and Frost (1946)
			Holder and Hand (1982)
		$CH_4 + C_2H_6$	*Deaton and Frost (1946)*
			McLeod and Campbell (1961)
			Holder and Grigoriou (1980)
C_2H_6 : 2 parameters	*Structure II*	$C_2H_6 + C_3H_8$	*Holder and Hand (1982)*
C_3H_8 : 2 parameters	*Structure II*	C_3H_8	*Deaton and Frost (1946)*
			Miller et al. (1946)
			Wilcox et al. (1941)
i-C_4H_{10} : 2 parameters	*Structure II*	i-C_4H_{10}	*Wu and Robinson (1976)*
			Schneider and Farrar (1968)
C_4H_{10} : 2 parameters	*Structure II*	$CH_4 + C_4H_{10}$	*Ng and Robinson (1977)*
N_2 : 4 parameters	*Structure II*	N_2	*Van Cleeff and Diepen (1960)*
			Van Cleeff and Diepen[36]
		$N_2 + C_3H_8$	*Ng et al. (1977/1978)*
N_2 : 4 parameters	*Structure I*	$CH_4 + N_2$	*Jhaveri and Robinson (1965)*

Finally, the dash line presents calculations of dissociation temperature when the fugacity of the empty hydrate is obtained from the conventional approach (equation 8.12) with parameters for equations (8.13) and (8.14) as previously, while the Langmuir constants (C_{mi}) are obtained from equation (8.8) with parameters as tabulated in table 8.1. As shown, the results are sensitive both to Langmuir values as well to the fugacity values of the empty hydrate. Therefore the parameters used in the Langmuir expression cannot be obtained from the literature, but should be regressed depending on the model used, in order to provide adequate calculations of dissociation data.

8.3. Prediction of gas phase water content for nitrogen – water and methane – water systems.

Data for equilibrium water content of gases are generally reported without the corresponding value of gas in the liquid, and vice versa; thus all data here are only gas phase data. Considering the most common needs of the gas industry, data above 380 K have not been included in the work. In total 484 experimental data for the two systems are available to the best of our knowledge, as can be seen in tables 8.3 and 8.4 for the systems water – nitrogen and water – methane, respectively.

The heavy phase that is in equilibrium with the gas phase is in most of the cases not reported. Since the basic experimental steps needed to determine the equilibrium water content of the gas are in general i): to saturate the gas at known T and P which are the equilibrium conditions and ii) analyze the water content, it is in principle possible to determine the heavy phase that equilibrates with the gas based on the pressure – temperature diagram of the water – gas system. For nitrogen – water system that three – phase data exist only at elevated pressures, the H-V-I line is extrapolated, based on model calculations, to lower pressures in order to distinguish among the phases (i.e. vapor – ice or vapor – hydrate). A typical pressure – temperature diagram for water-methane is illustrated in figure 8.4, presenting also the various types of phase equilibria. Gas phase water content measurements of three different authors at 100bar are also presented. The purpose of the modelling part is to evaluate the modelling approach presented in section 8.2 (i.e. calculated fugacities), by comparing the deviation (in temperature) of the heavy phase that equilibrates with the gas phase at given pressure and gas phase water content. Deviations between data and model are reported in terms of temperature and not water content which is then an input. This gives a better overview for the deviation than using water content, since the spread between the experimental water content is significant. Tables 8.3 and 8.4 summarize the results for water – nitrogen and water – methane systems, respectively.

Adequate predictions of the gas phase water content for both systems is achieved, as demonstrated in tables 8.3 and 8.4 for the systems water – methane and water – nitrogen, irrespectively the heavy phase that equilibrates with gas (i.e. liquid, hydrate or ice depending on the temperature and pressure of saturation). This indicates that the modeling approach provides reasonable fugacity calculations for each individual phase. In some cases, as for example the experimental measurements of Chapoy[24] the results obtained in this work deviate significantly from the actual measurements. Such a behavior is more likely to be attributed to the measurements, rather than the performance of the model for the following reason: The measurements of Chapoy[24] deviate significantly from other data at the same temperature and pressure. For example Althaus[16] and Chapoy[24], both using static cell for saturating the gas and GC analysis for measuring the water content, have very different results at 283K and 100bar (176 and 21 ppm, respectively). The value of Althaus[16] is in good agreement with Kosyakov[18] (150 ppm) and Frøyna[20] (173.8ppm) at the same temperature and pressure. Similar observations are valid for the measurements of Blanco[17] for nitrogen – water system. We believe that the experimental data of Chapoy[24] and Blanco[17] should be omitted, because they are inconsistent with all other experimental sources.

The calculations of CPA coupled with the modeling approach presented in section 8.2 for the ice or hydrate solid phase are very similar to the results obtained with the ISO standard GERG-water EoS, which indeed provides very accurate results in most of the cases. However the flexibility of using CPA for those binary systems relies on the fact that not only no binary interaction parameters are required, but also that calculations can be done over a wider temperature and pressure range, compared to the very strict limits of GERG-water model. Exactly due to the limitations in the temperature range, GERG-water model cannot be applied for temperatures higher than 313.15K; therefore experimental data at higher temperatures are not considered in the later case (see tables 8.3 and 8.4).

Figure 8.4 presents typical results for the system water – methane at 100bar. For comparison reasons the metastable phases are also presented with the CPA. As already mentioned GERG-water model enables equilibrium calculations of gas phase water-content with the most stable phase, treating the phase that equilibrates with gas as a “pseudo-liquid” phase. As figure 8.4 illustrates below 273.15K, where the gas phase equilibrates with a hydrate phase according to the temperature and pressure of the system, there is some scattering in data. One reason might be the experimental error in determining the gas phase water content. Another reason might be that the residence time of the sample under equilibration is not enough for obtaining equilibrium. Frøyna and Althaus followed the same experimental procedure with the difference that Althaus would leave the samples under equilibration for 24h while Frøyna only for 1h; the values of Frøyna at low temperatures are systematically higher than those of Althaus, as also presented in figure 8.4.

Even though for the calculations presented in tables 8.3 and 8.4 the heavy phase that equilibrates with gas is determined by the experimental temperature and pressure, CPA accurately predicts in most cases the stable phase that equilibrates with gas (as is the hydrate phase at low temperatures in figure 8.4), when using the gas phase water content as an input and optimizing the equilibrium temperature. The maximum temperature among the various types of equilibrium (vapour – liquid, vapour – ice or vapour – hydrate) is thermodynamically most stable.

Summarizing the performance of the two models, CPA provides similar and occasionally superior results compared to the GERG-water model. At elevated temperatures and still intermediate pressures (higher than 100bar), GERG-water model tends to slightly underestimate the calculated water content, as presented in figure 8.4. This becomes even more pronounced at elevated temperatures and pressures; at those conditions, where the liquid phase is the most stable, the prediction of the vapor-liquid equilibrium with the CPA EoS in superior, even if no binary interaction parameter is used.

Similar conclusions are obtained for the binary water – nitrogen system. Accurate calculations of the water content in the gas phase can be obtained with both models for low and intermediate pressures. However, for the binary water – nitrogen system, GERG-water model has the tendency to overestimate the water content in the gas phase at elevated pressures and temperatures, resulting to an inferior behavior compared to CPA. Calculations at 100bar are presented in figure 8.5.

The following summarize our observations:

1. For both systems, the prediction of the gas phase water content in equilibrium with the most stable phase is satisfactory with CPA. The modeling approach presented in this chapter enables, also, differentiation between the various heavy phases (i.e. liquid, ice or hydrate phase) that could equilibrate with the gas phase.
2. When ice or hydrate phase is the stable phase and for most of the literature data, the performance of CPA is very similar to GERG-water model. For high pressure measurements, where water condensates, the CPA model performs systematically better compared to GERG model based on all literature data.

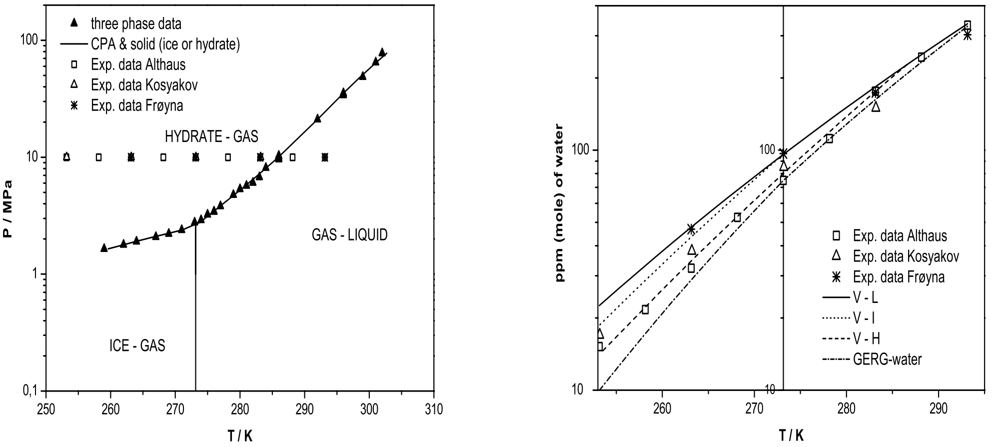


Figure 8.4. Prediction of the water content between the gas and a heavy phase for the binary system water – methane at 100bar with the CPA EoS. The performance of GERG-water model is also presented. For the CPA the metastable vapor –liquid (V-L), vapor-ice (V-I) or vapor-hydrate (V-H) phases are also presented.

3. Contrary to GERG –water model, where the actual temperature and pressure range for gas phase water content calculations is very limited and a binary interaction parameter is always required, the CPA EoS provides excellent predictions of water solubility in the gas phase. Figure 8.6 presents predictions (k_{12}=0.0) of water solubility in methane for a temperature range of 310 – 573K and a much extended pressure range up to 1000bar. The results are very accurate in all cases.

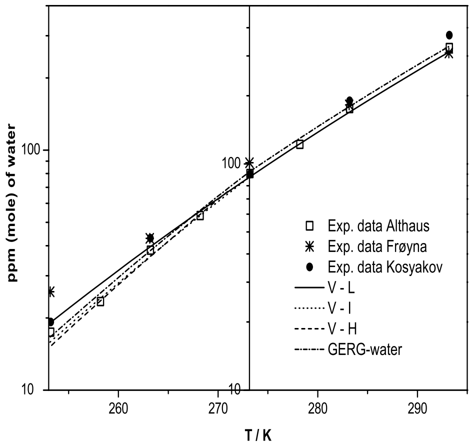


Figure 8.5. Prediction of the water content between the gas and a heavy phase for the binary system water – nitorgen at 100bar with the CPA EoS. The performance of GERG-water model is also presented. For the CPA the metastable vapor –liquid (V-L), vapor-ice (V-I) or vapor-hydrate (V-H) phases are also presented.

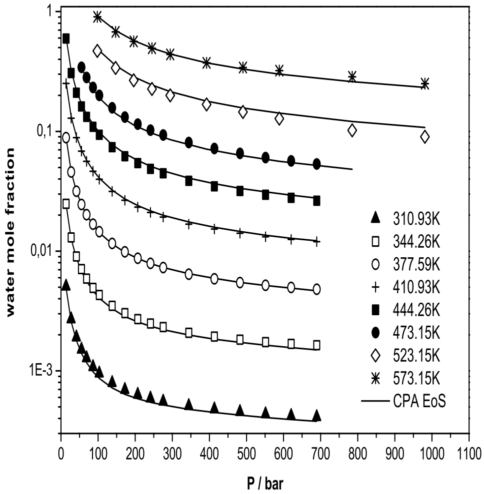


Figure 8.6. Prediction (k_{12}=0.0) of water content in methane for the water – methane binary system over an extended T and P range. Experimental data from Olds[14] and Sultanov[15].

Table 8.3. Predictions of gas phase water content with the CPA EoS and comparison to GERG model for the system water – nitrogen.

	T [K]	**P [bar]**	**NP**	**VLE (CPA)**	**NP**	**CPA + ice**	**NP**	**CPA + hydrate**	**GERG-water**
Reference	**min/max**	**min/max**	**Lw**	**AAD [K]**	**Ice**	**AAD [K]**	**Hydrate**	**AAD [K]**	**AAD [K]**
Althaus[16]	248/293	5/100	22	0.5	19	0.5	2	0.8	0.5
Blanco[17]	250/283	5/100	24	3.9	28	3.8	-	-	4.2
Kosyakov[18]	233/293	10/121	18	1.5	17	0.9	8	2.5	1.3
Bogoya[19]	258/288	30/60	8	1.4	6	1.1	-	-	1.4
Frøyna[20]	258/293	5/200	21	0.7	16	2.1	4	3.9	0.8
Rigby[21]	298/348	22/90	10	0.4	-	-	-	-	0.1[a]
Gillespie[22]	311	3/130	6	0.8	-	-	-	-	0.4

[a] for Rigby et.al. 3 experimental points at 298.15K were considered.

Table 8.4. Predictions of gas phase water content with the CPA EoS and comparison to GERG model for the system water – methane.

	T [K]	**P [bar]**	**NP**	**VLE (CPA)**	**NP**	**CPA + ice**	**NP**	**CPA + hydrate**	**GERG-water**
Reference	**min/max**	**min/max**	**Lw**	**AAD [K]**	**Ice**	**AAD [K]**	**Hydrate**	**AAD [K]**	**AAD [K]**
Althaus [16]	253/293	5/100	15	0.4	9	0.8	26	0.5	0.5
Kosyakov [18]	233/283	10/101	5	0.8	2	0.5	26	1.3	1.1
Aoyagi [23]	230/270	13/103	-	-	-	-	35	2.3	3.4
Chapoy [24]	283/318	10/351	39	5.9	-	-	-	-	6.5[b]
Bogoya [19]	258/288	30/60	5	1.4	-	-	9	1.8	1.0
Frøyna [20]	253/293	15/180	8	1.5	2	0.7	15	3.1	1.7
Olds [14]	310/377	13/206	27	0.9	-	-	-	-	0.5[c]
Sharma[25]	311/344	15/144	15	1.4	-	-	-	-	1.2[d]
Yarym[26]	313/338	25/125	10	1.8	-	-	-	-	0.4[e]
Yokoyama [27]	298/323	30/80	5	0.5	-	-	-	-	0.3[f]
Rigby [21]	298/373	23/93	12	0.2	-	-	-	-	0.2[g]
Gillespie[28]	323/348	14/138	6	0.7	-	-	-	-	-
Culberson[29]	311	52/249	4	2.5	-	-	-	-	2.9

[b] The experimental data from Chapoy et.al. were used up to 313K.

[c] From Olds et.al. 9 experimental data at 310K were considered.

[d] From Sharma et.al. 5 experimental data at 311K were considered.

[e] From Yarym et.al. 5 experimental points at 313K were considered.

[f] From Yokohama et.al. 2 experimental data at 298K were considered.

[g] From Rigby et.al. 3 experimental points at 298K were considered.

8.4. Multicomponent Mixtures

The performance of the models is further tested in 9 different gas mixtures. The % mol composition (dry basis) of each mixture as well as the temperature and pressure range of available experimental data is tabulated in table 8.5. It is assumed that compounds other than those reported in table 8.1 do not form hydrates for the CPA calculations. Such an assumption is not expected to influence the results, since the concentration of these components is very low for all the mixtures tested in this work, in order to dominate the behavior of the system. Althaus mixtures contain some higher components too in very small amounts. These have been lumped with n-C_5 in the calculations. It must be emphasized that the calculations using CPA are purely predictive (i.e. there are no interaction parameters between any of the components). This is as opposed to GERG which requires temperature dependent interaction parameters for water-carbon dioxide, water-methane and water-ethane, as Appendix 3 demonstrates.

Table 8.5 provides an overview of the performance of CPA EoS combined with the modeling approach presented in section 8.2 and a comparison to GERG-water model. In this table, temperature deviations for the most stable phase in equilibrium with the gas phase are presented. The phase envelope of the dry gas is calculated in order to check if the experimental data intersect the phase envelope or lie within a condense hydrocarbon phase region. For phase envelope calculations the SRK EoS was used. For this reason four experimental points are omitted (248.2 K, 253.2 K and 60 bar from the mixture E4 and 258.2K and 40 and 60 bar for the mixture E5).

As tabulated in table 8.5 the prediction of the gas phase water content is in all cases very satisfactory with the CPA EoS and very similar to GERG-water model. However, the CPA results are pure predictions (i.e. k_{12}=0), while the calculations performed with GERG-water model require at least a temperature independent interaction parameters for all binary systems, while in many cases, a temperature dependent binary interaction parameter is required. Figure 8.7 presents typical results with the CPA EoS and the GERG-model for the mixture with composition 93.22% C_1, 2.91% C_2, 0.71% C_3, 1.94% N_2, 0.85% CO_2, 0.135% n-C_4, 0.09% i-C_4, 0.1% C_5+ of dry basis, at 60bar and 100bar, respectively.

Table 8.5. Prediction of gas water content in equilibrium with the most stable phase for natural gas mixtures, expressed as temperature AAD in K.

Ref	Mixture Composition, mole % dry basis	T min/max [K]	Pmin/max [bar]	CPA	GERG-water
16	98.19% C_1, 0.56% C_2, 0.19% C_3, 0.84% N_2, 0.11% CO_2, 0.04% n-C_4, 0.03% i-C_4, 0.02% C_5+	253/288	5/100	0.6	0.5
16	93.22% C_1, 2.91% C_2, 0.71% C_3, 1.94% N_2, 0.85% CO_2, 0.135% n-C_4, 0.09% i-C_4, 0.1% C_5+	248/288	5/100	0.5	0.6
16	88.21%C_1, 8.36%C_2, 1.76% C_3, 0.91%N_2, 0.44% n-C_4, 0.29% i-C_4, 0.01% C_5+	258/288	5/100	0.4	0.8
16	86.35%C_1, 6.19% C_2, 1.55% C_3, 4.86%N_2, 0.17% CO_2, 0.31% n-C_4, 0.21% i-C_4, 0.19% C_5+	248/293	5/100	0.4	0.7
16	84.34%C_1, 8.72% C_2, 3.28% C_3, 0.80%N_2, 1.73% CO_2, 0.58% n-C_4, 0.31% i-C_4, 0.2% C_5+	258/288	5/100	0.8	0.9
16	83.84%C_1, 3.46% C_2, 0.66% C_3, 10.35%N_2, 1.29% CO_2, 0.13% n-C_4, 0.1% i-C_4, 0.14% C_5+	258/288	5/100	0.5	0.5
25	91.45% C_1, 8.55% N_2	310/344	14/140	0.9	1.0[k]
25	81.14% C_1, 18.86% N_2	310/344	14/140	1.0	1.2[k]
20	84.4% C_1, 10.0% C_2, 4.0% C_3, 1.0 % n-C_4, 0.6% i-C_4	263/293	15/60	1.0	1.1

[k] only experimental data at 310K were considered (5 points)

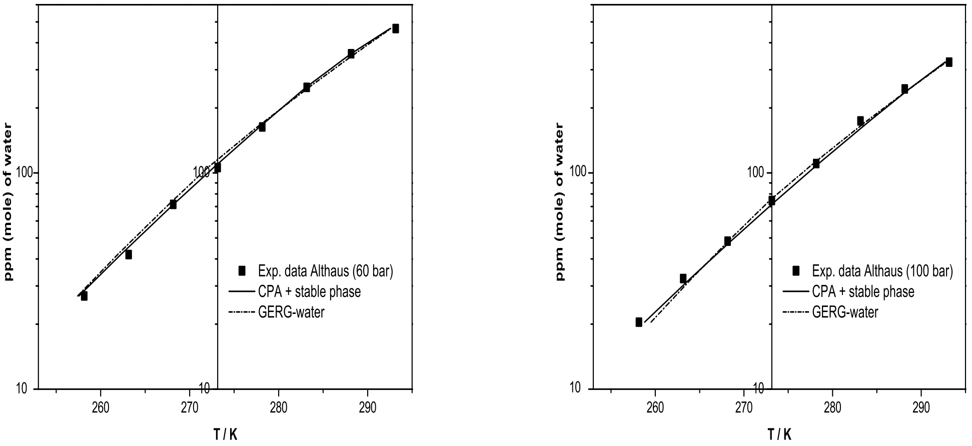


Figure 8.7. Prediction of the water content between a gas and a heavy phase with the CPA EoS for a natural gas mixture at 60bar and 100bar. The mixture has the following composition: 93.22% C_1, 2.91% C_2, 0.71% C_3, 1.94% N_2, 0.85% CO_2, 0.135% n-C_4, 0.09% i-C_4, 0.1% C_5+ of dry basis. For comparison purposes the GERG-water model is also presented.

8.5. Gas Hydrate predictions in the presence of Inhibitors

CPA is further tested for hydrate formation predictions of simple mixtures containing methane, ethane or propane and a hydrate inhibitor. In particular mixtures containing methanol, ethylene glycol (MEG) and tri-ethylene glycol (TEG) are considered. For the binary system of MEG – water ECR combining rule is used, with k_{12}=-0.115, since this is shown to provide adequate VLE and SLE calculations of water – MEG system. For the binary systems of water – methanol (used when mixtures contain methanol as inhibitor) two cases have been considered: ECR combining rule with k_{12}=-0.09 since this is shown to give satisfactory VLE results and ECR with k_{12}=-0.153, which is the binary interaction parameter optimized from SLE data. The reason for testing both values of k_{12} is two-fold: First to test the sensitivity of the calculations to methanol – water system and then to further validate if the binary interaction parameter obtained from SLE data can be used for gas hydrate calculations using inhibitor, since such chemicals shift the Vapor – Hydrate – Liquid equilibrium to lower temperatures. For water – TEG CR-1 rule with k_{12}=-0.211 is used, as in the absence of SLE data, this is shown to perform better for the VLE of TEG – water system, over a limited however temperature range that it is tested.

For MEG – methane system the binary interaction parameter used is k_{12}=0.134 (according to chapter 7), for methanol – propane the binary interaction parameter is obtained from the VLE of the system at 293K (k_{12}=0.026), and finally for methanol – methane the value of the binary interaction parameter is k_{12}=0.0134, according to Kontogeorgis et al.[30]. All the other binary interaction parameters are zero. Table 8.6 summarizes the results. The concentration of the inhibitor in the liquid phase is fixed to the one presented in table 8.6 for the PT flash calculations. Typical results for hydrate formation calculations in the presence of inhibitor are presented in figures 8.8 – 8.10.

The performance of the model is satisfactory in most of the cases over an extended pressure range. Somehow inferior results are obtained for all systems for the highest amount of inhibitor added. This can be due to several reasons. An obvious reason for the case of TEG is that the binary interaction parameter between water – TEG which is obtained from VLE data is not adequate enough for low temperatures (as shown in figure 8.8 the binary interaction parameter indeed influences the calculations). However this cannot entirely explain the similar behavior when methanol is used as an inhibitor. For such calculations, it is difficult to identify if the inferior performance is due to the liquid or vapor phase calculations from CPA, or if it is related to the parameters used for estimating the hydrate fugacity from equation (8.5). It is of interest to mention that similar calculations were recently presented by Li et.al.[11] using SAFT. Although in the work of Li et al.[11] the hydrate formation pressure is the optimized parameter, while in this work the hydrate formation temperature is being optimized, the performance of SAFT for water – methanol – methane system is inferior to CPA (the calculations with SAFT give an error of 11.5% in pressure for 35% wt of methanol and 18.5% for 50% wt of methanol).

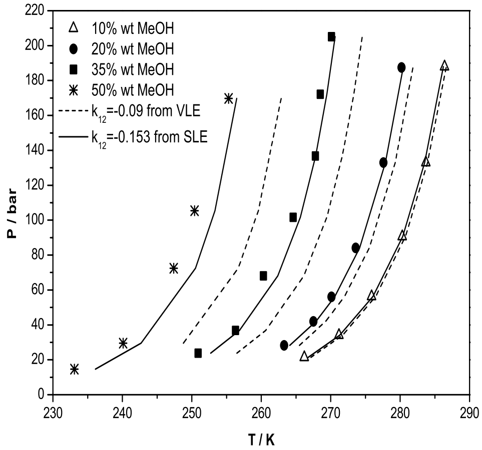
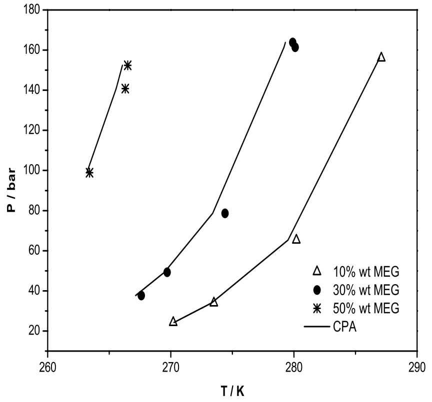


Figure 8.8. Prediction of methane hydrate formation in the presence of methanol as inhibitor.

Table 8.6. Hydrate formation temperature calculations with the CPA EoS

Gas	Inhibitor (%wt)	T min/max [K]	P min/max [bar]	AAD [K]	Ref
methane	10% methanol	266 – 286	21 – 188	0.2	31
	20% methanol	263 – 280	28 – 188	0.5	31
	35% methanol	251 – 270	24 – 205	1.0	32
	50% methanol	233 – 255	15 – 170	2.3	32
	10% MEG	270 – 287	24 – 156	0.3	33
	30% MEG	267 – 180	37 – 161	0.8	33
	50% MEG	263 – 266	99 – 152	1.0	33
	10% TEG	274 – 293	31 – 256	0.3	^{3}3
	20% TEG	275 – 293	44 – 399	0.4	34
	40% TEG	274 – 283	73 – 351	2.2	34
ethane	10% TEG	277 – 289	10 – 233	0.7	34
	20% TEG	274 – 289	8 – 363	0.8	34
	40% TEG	275 – 283	20 – 355	0.6	34
propane	5% methanol	272 – 275	2 – 64	0.5	32
	10% methanol	269 – 272	2 – 65	0.5	32
	35% methanol	250 – 253	1 – 98	2.1	32
	10% TEG	272 – 277	2 – 5	0.2	35
	20% TEG	271 – 275	2 – 5	0.7	35
	30% TEG	270 – 272	3 – 4	1.8	35



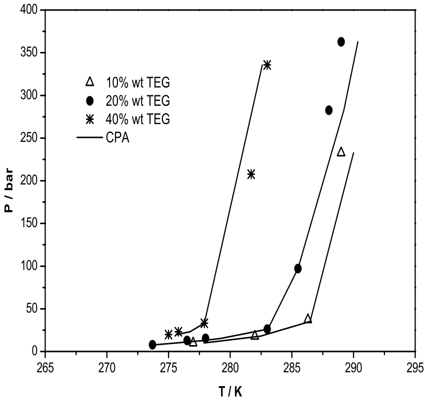


Figure 8.9. Prediction of methane hydrate formation in the presence of MEG as inhibitor.

Figure 8.10. Prediction of ethane hydrate formation in the presence of TEG as inhibitor.

8.6. Conclusions

In this chapter CPA coupled with a solid phase model, when required, is used to predict the gas phase water content for binary systems of water – methane, water – nitrogen and natural gas mixtures. A thermodynamically consistent modeling approach is implemented, using the CPA to obtain the fugacity of both the vapor and liquid phase, while the hypothetical empty hydrate phase is modeled as a solid phase.

Accurate predictions of the gas phase water content in equilibrium with a heavy phase are obtained for the systems tested. Furthermore, accurate differentiation of the stable heavy phase (i.e. liquid – vapor, vapor – ice or vapor – hydrate) was obtained. The performance of CPA is compared to GERG-water model. Even thought the results obtained with CPA are pure predictions, the comparison indicates that for the binary systems tested the performance of CPA is very similar to the ISO-standard GERG-water model at low pressures while becomes superior at elevated pressures and temperatures. The prediction of natural gas mixtures with CPA shows that reliable results can be obtained also for multicomponent systems studied, maintaining the simplicity in the model and completely eliminating the need of adjustable parameter.

Initial predictions of hydrate formation temperatures of simple mixtures in the presence of inhibitors suggest that CPA can provide acceptable results even when the number of binary interaction parameters is limited.

8.7. Literature Cited

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Chapter 9

Conclusions and Recommendations for Future Work

This chapter summarizes the main conclusions of this study and discusses areas of future research. In cases that preliminary calculations are done for areas of future interest, those are also included in the discussion.

The CPA model was initially applied to various types of phase equilibria of systems containing alcohols/glycols and water. Such molecules can self – associate but also cross – associate (solvate) with each other. For the calculations alcohols are considered as 2-site molecules while water and glycols as 4-site ones, in accordance to previous studies. It is concluded that a single and temperature independent binary interaction parameter suffices for VLE calculations over extensive temperature and pressure ranges, when ECR combining rule is used. The model can also correlate the LLE of water – heavy alcohols, while in this case CR-1 combining rule is found to perform best for adequate calculations of both solubilities with the same binary interaction parameter. It is concluded that a different binary interaction parameter and a different combining rule should be used for LLE and VLE calculations of higher alcohols – water systems, such as butanol – water or pentanol – water. SLE correlations are also very satisfactory for methanol – water and MEG – water systems with ECR, including also the modeling of the intermediate solid-complex phase. Even though for MEG – water the same binary interaction parameter obtained from VLE can be used, it was concluded that for methanol – water system the k_{12} obtained from VLE does not provide satisfactory results. The same was concluded for butanol – water SLE.

Even though the correlative performance of the model is very satisfactory and the use of temperature independent binary interaction parameters indicates an adequate built-in temperature dependency of the model, the values of the binary interaction parameters required for those complex mixtures with water are relatively high. Furthermore, different combining rules, which actually modify mathematically the association strength, are required. For these reasons, the choice of the active sites of water and alcohols is investigated. It is shown that water should be treated as a 4-site molecule, because only this choice provides satisfactory LLE correlations of water – alkanes.

A study of alcohols as a 3-site molecule and a comparison to the performance of the 2-site scheme concludes that overall VLE, LLE and SLE correlation results for alcohol – hydrocarbon systems are similar. The 2-site scheme perform systematically better only in the alcohol diluted area. The study of solvating alcohol-water systems concludes that the correlative performance of both schemes is also very similar. However in this case, a much lower value of the binary interaction parameter (k_{12}) or even no binary interaction parameter suffices for satisfactory calculations with the 3-site scheme for alcohols. Another limitation of the 3-site scheme is revealed in the case of partially immiscible systems of water with heavy alcohols, where the model fails to simultaneously correlate both solubilities with the same binary interaction parameter. A comparison of the predictive performance of the model to multicomponent multiphase equilibria of systems containing methanol concludes that superior predictions of methanol partition coefficients are obtained with the 2-site scheme for alcohols. Hence, the only advantage obtained with the 3-site molecule for alcohols is the lower values of binary interaction parameters for VLE of water – alcohol systems. As a conclusion alcohols should be treated as 2-site molecules with CPA.

The low value of the interaction parameter (k_{12}) for water – alcohols should be attributed to the extra active site in the molecule of alcohols when a 3-site molecule is assumed. For the evaluation of the 3-site scheme for alcohols in this work, the bonding (association) strength of each of the two lone pairs of alcohols to the hydrogen atom is assumed to be equal. As a future suggestion it might be of interest to investigate the performance of the 3-site scheme for alcohols, when the bonding strength of each of the two lone pairs in the molecule of alcohol to a hydrogen atom is weighted differently. A first assumption could be that the bonding strength of one lone pair is half of the value of the other.

It is of importance to mention that the phenomenon of the high k_{12} values for alcohol – water VLE calculations is rather related to the presence of water and should not be generalized as an incapability of the model to describe phase equilibria of solvating systems (and thus a high k_{12} value is required to correct for this incapability). Preliminary calculations for alcohol – alcohol binary systems demonstrate that CPA, using both association schemes for alcohols and either CR-1 or ECR, provides satisfactory results with the use of a very low binary interaction parameter, even for asymmetric systems, such as methanol – octanol. Results are presented in figures 9.1 for the VLE of ethanol – butanol and in figure 9.2 for the VLE of methanol – octanol system.

The CPA model is applied to complex systems containing aromatics or olefinic hydrocarbons. These components do not self-associate but form hydrogen bonds in the presence of an associating component such as water. A modification of the CR-1 rule (mCR-1) is developed for correlating these systems. The use of mCR-1 requires however an additional adjustable parameter, the cross –

association volume and consequently increases the number of adjustable parameters to two (including the k_{12} in the physical term) in order to account for these effects. It is concluded that for water – aromatic/olefinic hydrocarbons the model should account for the solvation, in order to simultaneously correlate both solubilities. Furthermore, a generalized correlation for the binary interaction parameter based on the carbon number of the hydrocarbon is successfully used for water – alkane LLE calculations. This binary interaction parameter in the physical term can be used for the homomorph aromatic/olefinic hydrocarbon – water system (i.e. the same carbon number as the alkane). This approach reduces the adjustable parameters for LLE calculations of water – aromatic/olefinic hydrocarbons to one (the cross-association volume in the expression of mCR-1). Accounting for the solvation is concluded to be less important for alcohols - aromatic hydrocarbons binary systems. Especially for ethanol – aromatic hydrocarbons the use of a binary interaction parameter (k_{12}) can adequately account for the solvation, as calculations of VLE and infinite dilution activity coefficients indicate. LLE prediction results of ternary water – alcohol – aromatics further validate the successful extension of the model to aromatic hydrocarbons with the mCR-1 rule.

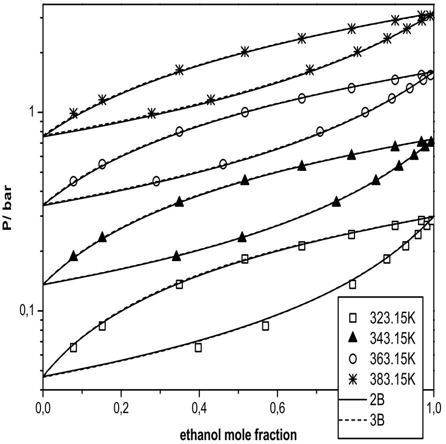


Figure 9.1. VLE calculations of ethanol – butanol using ECR and 2B scheme with k_{12}=0.0 (solid line) or ECR and 3B scheme with k_{12}=0.0(dash line). Experimental data are from Kharin et al.[1]

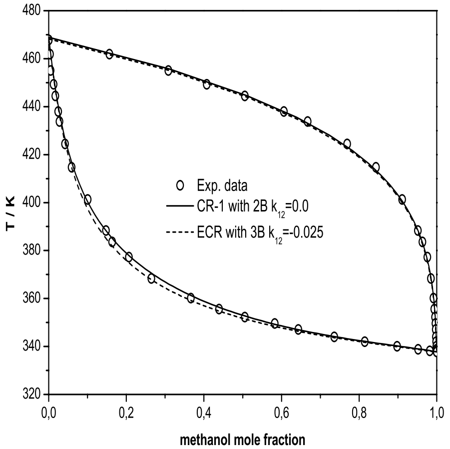


Figure 9.2. VLE calculations for methanol-octanol using CR1 and 2B scheme with k_{12}=0.0 (solid line) or ECR and 3B scheme with k_{12}=-0.025 (dash line). Experimental data are from Arce et al.[2]

New experimental liquid – liquid equilibrium data of four binary systems containing glycols + aromatic hydrocarbons and three ternary mixtures of glycols + water + aromatic hydrocarbons are measured at atmospheric pressure. The traces of glycols and hydrocarbons are analyzed using GC while the water content in the hydrocarbon phase is measured using KF titration. GC and KF titration are used for analyzing water content in the polar phase and results are found to be within the uncertainty of the measurements. A comparison to available experimental data suggests that the obtained measurements are reliable. Accounting for the solvation between glycols and aromatic hydrocarbons is concluded to be important for satisfactory calculations of these systems, while mCR-1 is concluded to provide adequate correlations of glycol – aromatic hydrocarbon systems and reliable predictions of ternary glycol – water – aromatic hydrocarbon mixtures.

The performance of SRK using Huron – Vidal mixing rule and modified NRTL as an activity coefficient model is studied. LLE of water – aliphatic/aromatic hydrocarbons and LLE of glycol - aliphatic/aromatic hydrocarbons are considered. It is concluded that three parameters in the modified NRTL model do not satisfactorily represent the temperature dependency of the solubility of water when simultaneously fitted both to the water solubility in the hydrocarbon phase and the hydrocarbon solubility in the aqueous phase. For LLE correlations of glycols – hydrocarbons the model correlates satisfactorily the hydrocarbon solubility in the glycol phase but provides inferior calculations for the glycol solubility in the hydrocarbon phase. The opposite occurs with CPA. Predictions of multicomponent multiphase equilibria using MEG as a hydrate inhibitor are concluded to be accurate with SRK using Huron – Vidal mixing rule. The results are compared to the performance of CPA and it is concluded that CPA provides overall superior calculations of water and glycol solubilities in the liquid hydrocarbon phase. Furthermore, CPA uses less binary parameters compared to SRK with Huron – Vidal mixing rules.

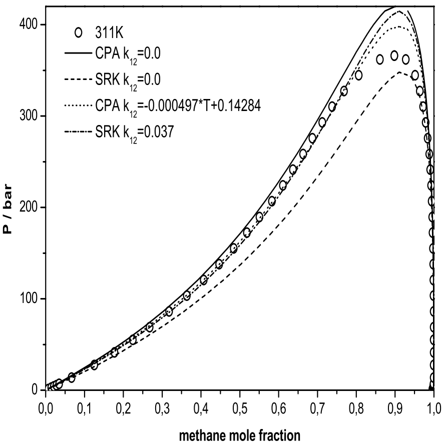
For the calculations of the multicomponent mixtures, a temperature independent binary interaction parameter for water-alcohol or water-glycol binary pair is used with CPA. The successful performance of CPA to multicomponent multiphase equilibria suggest that the model can be used for phase equilibria calculations at several temperature and pressure conditions based on the temperature independent parameters suggested in this work.

GERG-water model was recently suggested by GERG as an ISO-standard model for gas phase water content calculations. CPA has been coupled with a solid phase model and gas phase water content predictions (using k_{12}=0 for water - alkane) are performed for water – nitrogen, water – methane and selected natural gas mixtures, providing results very similar and occasionally better (for high pressure VLE) to GERG-water. Preliminary results also suggest that the modeling approach presented in this thesis provides satisfactory predictions of gas hydrate formation conditions. The method should be further validated for predictions of gas hydrate formation conditions of real natural gas mixtures, in cases that experimental data are available. Given that most natural gas mixtures have a high CO_2 concentration, which cannot be ignored, CO_2 should be first studied with CPA.

For computing the empty hydrate fugacity, the hypothetical empty hydrate phase is assumed to be a solid phase. This approach might be sensitive to specific cases, for the reason that the fugacity of the empty hydrate phase is totally independent from the EoS used. On the other hand the traditional approach for modeling the empty hydrate phase is related to the fugacity of the pure liquid water which is calculated from an EoS. Hence, when computing vapor – liquid – hydrate equilibria, the resulting equation will be a function of the activity coefficient which might be more flexible for specific cases. For this reason it would be of interest to compare the different approaches for modeling the empty hydrate fugacity in gas hydrate formation predictions of multicomponent systems.

An alternative approach for phase equilibria calculations of mixtures with acetone is presented in this thesis, assuming that acetone is a self-associating component and thus modeled as a 2-site molecule. Initial results suggest that this is a promising engineering alternative instead of adding a polar term. Including a polar term, which would be consistent to the physical picture of acetone and ketones in general, could be a future challenge for CPA. This would also be an interesting test for the behavior of the model in cases of components which are polar and associating.

It would be of interest to investigate the performance of the model when the CPA parameters for hydrocarbons are not fitted to vapor pressure and liquid density data, but obtained from the conventional approach, using the critical temperature, critical pressure and the acentric factor. Such an investigation should include phase equilibria calculations of asymmetric hydrocarbon mixtures, systems of hydrocarbons with water/alcohols/glycols and especially the sensitive LLE cases. The advantage of using the latter approach is that existing characterization methods could be directly combined with the model and that in-house industrial databases with interaction parameters for alkane mixtures can be used. It is recently shown in the literature[3,4] that PR EoS provides superior VLE prediction and correlation results of highly asymmetric alkane systems, when the parameters are fitted to vapor pressure and liquid density data. Such a study should be also performed for the SRK EoS, since the results with the PR EoS are not necessarily valid for the CPA



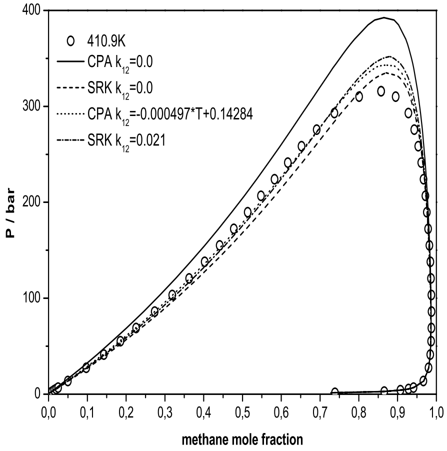
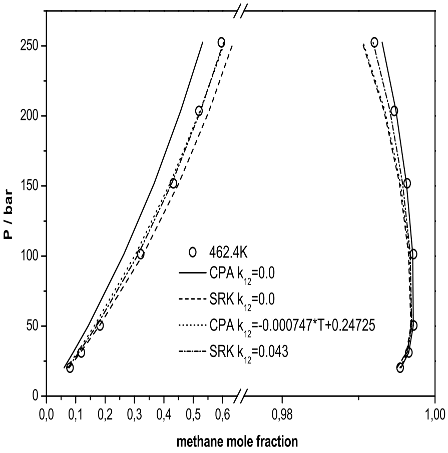


Figure 9.3. VLE of methane – n-C_{10} at 310.9K. Exp. data from Reamer et al.[6]

Figure 9.4. VLE of methane – n-C_{10} at 410.9K. Exp. data from Reamer et al.[6]



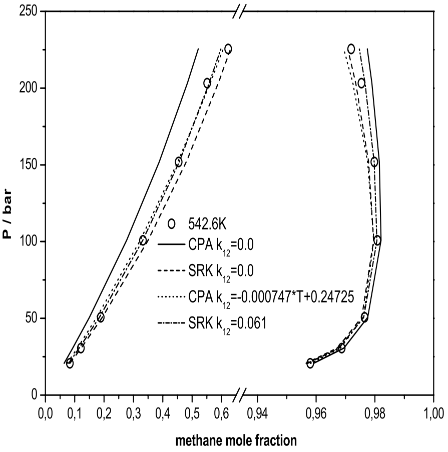


Figure 9.5. VLE of methane – n-C_{16} at 462.4K. Exp. data from Lin et al.[7]

Figure 9.6. VLE of methane – n-C_{16} at 542.6K, Exp. data from Lin et al.[7]

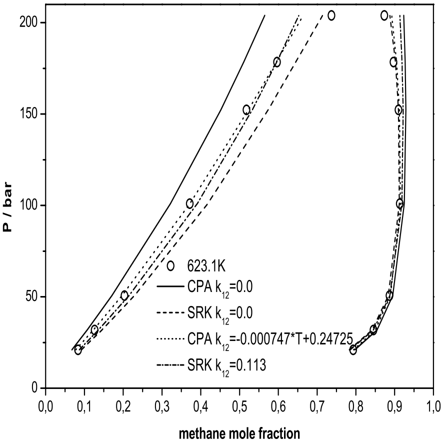


Figure 9.7. VLE of methane – n-C_{16} at 623.1K, Exp. data from Lin et al.[7]

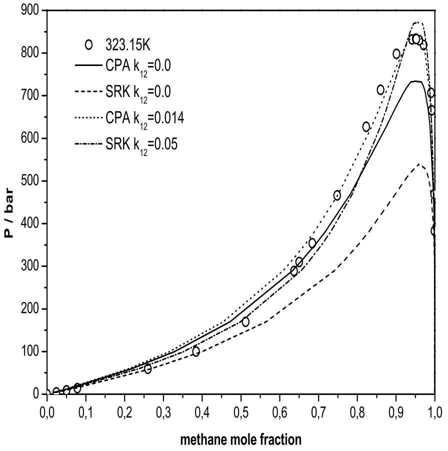


Figure 9.8. VLE of methane – n-C_{20} at 323.1K, Exp. data from Van der Kooi et al.[8]

(or SRK EoS) for two reasons: i) the critical properties and the acentric factor of light hydrocarbons (methane and ethane) are used for CPA calculations and this might influence the results and ii) the fugacity coefficients with SRK EoS are more accurate compared to PR EoS[5]. Some preliminary VLE calculations of methane – alkanes are presented in figure 9.3 – 9.10.

For all calculations the CPA parameters for methane are obtained using critical properties. When SRK is used, the critical properties and the acentric factor of the heavy alkane are used for the calculations, while when CPA is used the pure component parameters (fitted to vapor pressure and liquid density data) are used. Our preliminary calculations suggest that CPA can correlate the VLE of methane-decane and methane-hexadecane binary mixtures at different temperatures using a temperature dependent binary interaction parameter, while providing results similar to those reported by Voutsas[5] with PR-fit (fitted to vapor pressure and liquid density) and optimizing the binary interaction parameters per isotherm.

Ways to decrease the number of CPA adjustable parameters should be investigated, as for example incorporation of spectroscopic data.The co-volume parameter b which is the only of the five CPA parameters present in both the physical (SRK) and the association (Wertheim) part seems to be constant among the various sets, largely independent of the starting values of the regression.

Moreover, b seems to be related for all compounds studied to the van der Waals volume, V_w, as can be seen in figure 9.9, resulting to the equation:

$$b = 0.0018 * V_W - 0.0134$$

This equation can be used for reducing the number of pure parameters to be adjusted. The validity of this equation to heavy alkanes discussed previously would be of interest to investigate, since this is known to be valid up to n-eicosane that CPA parameters exist.

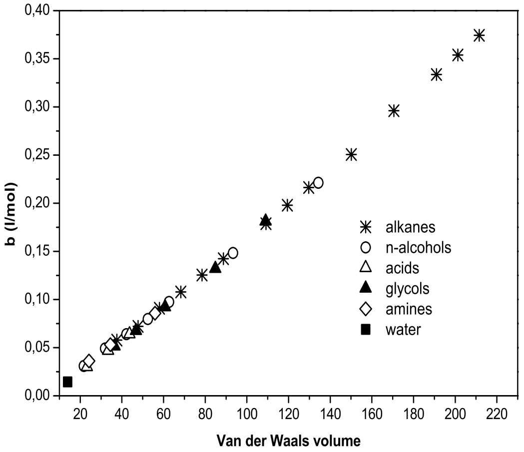


Figure 9.9. The co-volume parameter of CPA against the van der Waals volume for a variety of compounds

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List of symbols

α_{ij}	non-randomness parameter of molecules of type i around a molecule of type j
$\alpha_{mk}, \alpha_{mk,1}$	UNIFAC temperature dependent parameters, K
$\alpha_{mk,2}, \alpha_{mk,3}$	UNIFAC temperature dependent parameters, K^{-1}
a_0	parameter in the energy term (a), bar l^2 mol^{-2}
A_i	site A in molecule i
$A_{m,i}$	parameter in Langmuir constant, K bar^{-1}
A_1, A_2, A_3	parameters in GERG model for water
B_j	site B in molecule j
$B_{m,i}$	parameter in Langmuir constant, K
b	co-volume parameter, l mol^{-1}
c_1	parameter in the energy term (a)
$C_{m,i}$	Langmuir constant for component i in cavity m,
f	fugacity, bar
G^E	Excess Gibbs energy
g_{ji}/R	Huron – Vidal energy parameter, characteristic of the $j-i$ interaction, K
k	Boltzmann constant, J K^{-1}
k_{12}	binary interaction parameter
k_{ij}	binary interaction parameter
$k_{ij,o}, k_{ij,1}$	binary interaction parameters for water – gases in GERG model
$g(V_m)^{ref}$	radial distribution function
P	pressure, bar
Q_1, Q_2, Q_3	Mathias – Copeman parameters
Q_k	surface area parameter for group k
r	radial distance from the center of the cavity, Å
R	gas constant, bar l mol^{-1} K^{-1}
R_k	volume parameter for group k
R_i	the radius of cage i, Å
T	temperature, K

T_r	reduced temperature (T / T_c)
T_c	critical temperature, K
T_0	arbitrary temperature for UNIFAC, here 298.15K
$T_{m,i}$	melting temperature of the component i, K
V_m	molar volume, l mol^{-1}
V_W^{ICE}	molar volume of ice, l mol^{-1}
$W(r)$	cell potential function, J
x_i	liquid mole fraction of component i
y_i	vapor mole fraction of component i
X_{A_i}	fraction of A -sites on molecule i that do not form bonds with other active sites
X	monomer fraction
z	lattice co-ordination number
$\Delta \mathrm{H}_i^{fus}$	heat of fusion of the component i at the melting temperature, J mol^{-1}
ΔCp_i	heat capacity change of the component i at the melting temperature, J mol^{-1} K^{-1}
$\Delta\mu_w^0$	chemical potential difference between the empty hydrate and pure liquid water, J mol^{-1}
$\Delta h_w^{EH-L_0}$	enthalpy differences between the empty hydrate lattice and liquid water, J mol^{-1}
$\Delta V_w^{EH-L_0}$	molar volume differences between the empty hydrate lattice and liquid water, J mol^{-1}
T^{ref}	reference temperature, K
K	chemical equilibrium constant
K^{ref}	chemical equilibrium constant at the reference temperature

Greek Letters

$\beta^{A_iB_j}$	association volume parameter between site A in molecule i and site B in molecule j
γ_i^C	combinatorial part of activity coefficient for the component i
γ_i^r	combinatorial part of activity coefficient for the component i
Γ_k	activity coefficient of group k at mixture composition

Γ_k^i	activity coefficient of group k at a group composition of pure component i
$\varepsilon^{A_iB_j}$	association energy parameter between site A in molecule i and site B in molecule j, bar l mol^{-1}
η	the reduced fluid density
Δ	association strength, l mol^{-1}
ω	acentic factor
ω_i	modified volume fraction of the component i
ν_{ki}	number of groups of type k in molecule i
θ_i	surface area fraction for component i in the mixture
τ_{ji}	Boltzmann factor
Θ	occupancy of cavity m by component i
ν_i	number of cavities of type i

List of Abbreviations

AAD%	average absolute deviation ($AAD\% = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(\frac{x_{\exp,i} - x_{calc,i}}{x_{\exp,i}}\right)\cdot 100$) for a property x
BETCR	fitted cross-association volume parameter with mCR-1
Calc	calculated
CPA	Cubic – Plus – Association equation of state
DEG	diethylene glycol
ECR	Elliott combining rule
EoS	equation of state
Exp	experimental
GERG	Group Européen de Recherche Gazière
HV	Huron – Vidal mixing rule
LLE	liquid – liquid equilibrium
mCR-1	modified CR-1 combining rule for the CPA equation of state
MEG	(mono)ethylene glycol
NA	not available
NP	number of data points

TEG	tri-ethylene glycol
SAFT	Statistical Association Fluid Theory
SLE	Solid – liquid equilibrium
SRK	Soave – Redlich – Kwong equation of state
UNIFAC	Universal Quasi Chemical Functional Group Activity Coefficient
VLE	Vapor – liquid equilibrium
VLLE	Vapor – liquid – liquid equilibrium
$\Delta P\%$	average absolute percentage error ($\Delta P\% = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(\frac{P_{\exp,i} - P_{calc,i}}{P_{\exp,i}}\right)\cdot 100$) in bubble – point pressure *P* of component *i*.
Δy	average absolute deviation ($\Delta y = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(y_{\exp,i} - y_{calc,i}\right)$) in the vapor phase mole fraction of component i.
$\Delta \rho\%$	average absolute deviation ($\Delta \rho\% = \frac{1}{NP}\sum_{i=1}^{NP} ABS\left(\frac{\rho_{\exp,i} - \rho_{calc,i}}{\rho_{\exp,i}}\right)\cdot 100$) in the liquid density of component i.

APPENDIX A. Calculation of fugacity coefficients with CPA EoS

Appendix A presents all required equations for the calculation of the fugacity coefficient with the CPA EoS. The fugacity coefficient ϕ_i of a component i in a mixture is given by:

$$RT\ln\phi_i = \left(\frac{\partial A^r}{\partial n_i}\right)_{T,V,n_j} - RT\ln Z \tag{A.1}$$

A^r is the residual Helmholtz energy for the mixture and Z is the compressibility factor, defined as:

$$Z = \frac{PV}{nRT} \tag{A.2}$$

The CPA EoS combines the SRK EoS with the association term, derived from Wertheim's first order perturbation theory, hence:

$$A^r(T,P,n) = A^r_{SRK}(T,P,n) + A^r_{association}(T,P,n) \tag{A.3}$$

According to Michelsen and Mollerup[1] the fugacity coefficient for the SRK term can be calculated as follow:

$$\frac{A^r_{SRK}(T,V,n)}{RT} = -n\ln(1-\frac{B}{V}) - \frac{D(T)}{RTB}\ln(1+\frac{B}{V}) \tag{A.4}$$

V is the total volume of the system, while:

$$nB = n^2 b = \sum_i n_i \sum_j n_j b_{ij} \tag{A.5}$$

$$D(T) = n^2\alpha = \sum_i n_i \sum_j n_j \alpha_{ij}(T) \tag{A.6}$$

$$n = \sum_i n_i$$

Equation (A.6) is similar to equation (1.9) presented in chapter 1. The reason for using $D(T)$ instead of $\alpha(T)$ is to be consistent with the symbols used by Michelsen and Mollerup[1]. The classical one fluid Van der Waals mixing rules are used for the energy ($\alpha(T)$) and co-volume parameter (b):

$$\alpha_{ij}(T) = \sqrt{\alpha_i(T)\alpha_j(T)}(1-k_{ij}) \tag{A.7}$$

$$b_{ij} = b_{ji} = \frac{1}{2}(b_{ii} + b_{jj}) \tag{A.8}$$

As a result of equation (A.8), equation (A.5) reduces to:

$$B = \sum_i n_i b_{ii} \tag{A.9}$$

Assuming that:

$$\frac{A^r_{SRK}(T,V,n)}{RT} = -n\ln(1-\frac{B}{V}) - \frac{D(T)}{RTB}\ln(1+\frac{B}{V}) = F^{SRK} \tag{A.10}$$

$$g(V,B) = \ln(1-B/V) \tag{A.11}$$

$$f(V,B) = \frac{1}{RB}\ln(1+B/V) \tag{A.12}$$

Inserting equations (A.11) and (A.12) to equation (A.10) the resulting equation for F^{SRK} is:

$$F^{SRK} = ng(V,B) - \frac{D(T)}{T}f(V,B) \tag{A.13}$$

Hence for the calculation of the fugacity coefficient ϕ_i of a component i for the SRK term (equation A.1) the derivative of the function F^{SRK} is required:

$$\left(\frac{\partial F^{SRK}}{\partial n_i}\right)_{T,V,n_j} = F_n + F_B B_i + F_D D_i \tag{A.14}$$

Where:

$$\begin{aligned} F_n &= -g = -\ln(1-B/V) \\ F_B &= -ng_B - \frac{D(T)}{T}f_B \end{aligned} \tag{A.15}$$

With:

$$\begin{aligned} g_B &= -\frac{1}{V-B} \\ f_B &= -\frac{f + Vf_V}{B} \\ f_V &= -\frac{1}{R(V+B)} \\ F_D &= -\frac{f}{T} \end{aligned} \tag{A.16}$$

B_i and D_i are the composition derivatives of the energy term (eq. A.6) and the co-volume term (eq. A.9), given by the following equation:

$$B_i = \frac{2\sum_j n_j b_{ij} - B}{n} \qquad \text{(A.17)}$$
$$D_i = 2\sum_j n_j \alpha_{ij}$$

The Association term of the CPA EoS

The contribution of residual Helmholtz energy for the mixture for the association term $A^r_{association}(T,P,n)$ could be estimated, based on the approach proposed by Michelsen and Hendriks[2]. The authors introduced a Q function for the calculation of the derived properties of the association term, taking advantage of the fact that the association contribution to the Helmholtz energy is in itself the result of a minimization. By considering the Q function given by:

$$Q(n,T,V,X) = \sum_i n_i \sum_{A_i} (\ln X_{A_i} - X_{A_i} + 1) - \frac{1}{2V}\sum_i \sum_j n_i n_j \sum_{A_i} \sum_{B_j} X_{A_i} X_{B_j} \Delta^{A_i B_j} \qquad \text{(A.18)}$$

In equation (A.18) X_{A_i} is the fraction of A-sites on molecule i that do not form bonds with other active sites, n is the total composition of the mixture and V is the total volume. The association contribution of CPA EoS equals the value of Q at a stationary point with respect to the site fractions X. The conditions that apply at a stationary point are

$$\frac{\partial Q}{\partial X_{A_i}} = 0, \text{ for all sites} \qquad \text{(A.19)}$$

By differentiating equation (A.18)

$$n_i\left(\frac{1}{X_{A_i}} - 1\right) - \frac{1}{V} n_i \sum_j n_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j} = 0 \qquad \text{(A.20)}$$

Which yields:

$$\frac{1}{X_{A_i}} = 1 + \frac{1}{V}\sum_j n_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j} \qquad \text{(A.21)}$$

The value of Q at a stationary point (sp) is:

$$Q_{sp}=\sum_i n_i \sum_{A_i}(\ln X_{A_i}-X_{A_i}+1)-\frac{1}{2}\sum_i n_i \sum_{A_i} X_{A_i}\left(\frac{1}{V}\sum_j n_j \sum_{B_j} X_{B_j}\Delta^{A_iB_j}\right)\Rightarrow$$

$$Q_{sp}=\sum_i n_i \sum_{A_i}(\ln X_{A_i}-X_{A_i}+1)-\frac{1}{2}\sum_i n_i \sum_{A_i} X_{A_i}\left(\frac{1}{X_{A_i}}-1\right)\Rightarrow \tag{A.22}$$

$$Q_{sp}=\sum_i n_i \sum_{A_i}(\ln X_{A_i}-\frac{1}{2}X_{A_i}+\frac{1}{2})=\frac{A^r_{association}(T,P,n)}{RT}$$

In order to proceed to the calculation of the fugacity coefficient from the association term the chain rule should be used. According to the chain rule the derivative of Q_{sp} with respect to n_i is given by the following equation:

$$\frac{\partial Q_{sp}}{\partial n_i}=\left.\frac{\partial Q}{\partial n_i}\right|_X+\sum_i\sum_{A_i}\frac{\partial Q}{\partial X_{A_i}}\frac{\partial X_{A_i}}{\partial n_i} \tag{A.23}$$

At the stationary point however, the derivatives $\frac{\partial Q}{\partial X_{A_i}}$ are by definition zero, meaning that the fugacity coefficient for the association term can now be calculated using the explicit derivative of Q with respect to n_i:

$$\frac{\partial}{\partial n_i}\left(\frac{A^r_{association}}{RT}\right)_{T,P,n_j}=\frac{\partial}{\partial n_i}\left(\sum_i n_i\sum_{A_i}(\ln X_{A_i}-X_{A_i}+1)-\frac{1}{2}\sum_i n_i\sum_{A_i}X_{A_i}\left(\frac{1}{V}\sum_j n_j\sum_{B_j}X_{B_j}\Delta^{A_iB_j}\right)\right)_{T,P,n_j}=$$

$$\sum_{A_i}(\ln X_{A_i}-X_{A_i}+1)-\frac{1}{2V}\frac{\partial}{\partial n_i}\left(\sum_i\sum_j n_in_j\sum_{A_i}\sum_{B_j}X_{A_i}X_{B_j}\Delta^{A_iB_j}\right)-\frac{1}{2V}\sum_i\sum_j n_in_j\sum_{A_i}\sum_{B_j}X_{A_i}X_{B_j}\frac{\partial\Delta^{A_iB_j}}{\partial n_i}=$$

$$\sum_{A_i}(\ln X_{A_i}-X_{A_i}+1)-\frac{2}{2V}\sum_j n_j\sum_{A_i}\sum_{B_j}X_{A_i}X_{B_j}\Delta^{A_iB_j}-\frac{1}{2V}\sum_i\sum_j n_in_j\sum_{A_i}\sum_{B_j}X_{A_i}X_{B_j}\frac{\partial\Delta^{A_iB_j}}{\partial n_i}$$

When the yielding equation is combined with equation (A.21)

$$\frac{\partial}{\partial n_i}\left(\frac{A^r_{association}}{RT}\right)_{T,P,n_j}=\sum_{A_i}(\ln X_{A_i}-X_{A_i}+1)-\sum_{A_i}X_{A_i}\left(\frac{1}{X_{A_i}}-1\right)-\frac{1}{2V}\sum_i\sum_j n_in_j\sum_{A_i}\sum_{B_j}X_{A_i}X_{B_j}\frac{\partial\Delta^{A_iB_j}}{\partial n_i}=$$

$$\sum_{A_i}\ln X_{A_i}-\frac{1}{2V}\sum_i\sum_j n_in_j\sum_{A_i}\sum_{B_j}X_{A_i}X_{B_j}\frac{\partial\Delta^{A_iB_j}}{\partial n_i}$$

For the calculation of the derivative $\frac{\partial\Delta^{A_iB_j}}{\partial n_i}$ one has to consider that for CPA the function of the cross – association strength is given by the equation:

$$\Delta^{A_iB_j} = g(1/V_m)^{ref}\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right)-1\right]b_{ij}\beta^{A_iB_j} = g(n,V)\lambda(T) \tag{A.24}$$

Hence the derivative can be calculated as follow:

$$\frac{\partial\Delta^{A_iB_j}}{\partial n_i} = \frac{\partial g}{\partial n_i}\lambda = \frac{\partial \ln g}{\partial n_i}g\lambda = \Delta^{A_iB_j}\frac{\partial \ln g}{\partial n_i} \tag{A.25}$$

Therefore:

$$\frac{\partial}{\partial n_i}\left(\frac{A^r_{association}}{RT}\right)_{T,P,n_j} = \sum_{A_i}\ln X_{A_i} - \frac{1}{2V}\sum_i\sum_j n_i n_j \sum_{A_i}\sum_{B_j} X_{A_i}X_{B_j}\Delta^{A_iB_j}\frac{\partial \ln g}{\partial n_i} \tag{A.26}$$

Combining equation (A.26) with equation (A.21) the resulting equation is:

$$\frac{\partial}{\partial n_i}\left(\frac{A^r_{association}}{RT}\right)_{T,P,n_j} = \sum_{A_i}\ln X_{A_i} - \frac{1}{2}\sum_i n_i \sum_{A_i}(1-X_{A_i})\frac{\partial \ln g}{\partial n_i} \tag{A.27}$$

Hence for the calculation of the contribution of the association term, the derivative of g with respect to mole number n_i is required. Given that for the CPA EoS:

$$g(V,n) = \frac{1}{1-1.9\eta}\text{, where } \eta = \frac{B}{4V} \tag{A.28}$$

B is given by equation (A.9)

$\frac{\partial g}{\partial n_i} = \frac{\partial g}{\partial B}Bi$, where B_i can be calculated from equation (A.17), while:

$$\frac{\partial g}{\partial B} = 0.475V\left(\frac{1}{V-0.475B}\right)^2 \tag{A.29}$$

Calculation of volume

For the calculation of the fugacity coefficient ϕ_i of a component i in a mixture, the total volume is required, which can be calculated using a Newton – Raphson iteration method. The volume corresponding to a specific pressure, temperature and mixture composition can be calculated from the pressure equation:

$$P = \frac{nRT}{V} - \left(\frac{\partial A^r}{\partial V}\right)_{T,n} = \frac{nRT}{V} - \left(\frac{\partial A^r_{SRK}}{\partial V}\right)_{T,n} - \left(\frac{\partial A^r_{association}}{\partial V}\right)_{T,n} \tag{A.30}$$

From equation (A.10) the expression of the SRK term:

$$\left(\frac{\partial A^r_{SRK}}{\partial V}\right)_{T,n} = RT\left(\frac{\partial F^{SRK}}{\partial V}\right) \tag{A.31}$$

From equation (A.22) the expression of the association term is:

$$\left(\frac{\partial A^r_{association}}{\partial V}\right)_{T,n} = RT\left(\frac{\partial Q_{SP}}{\partial V}\right)_{T,n} \tag{A.32}$$

Inserting equation (A.31) and (A.32) into equation (A.30) the equation of the total pressure is:

$$P = \frac{nRT}{V} - RT\left(\frac{\partial F^{SRK}}{\partial V}\right)_{T,n} - RT\left(\frac{\partial Q_{SP}}{\partial V}\right)_{T,n} \tag{A.33}$$

Following the methodology presented by Michelsen and Mollerup[1], the necessary equations for the estimation of the contribution of the physical term are:

$$\left(\frac{\partial F^{SRK}}{\partial V}\right)_{T,n} = F_V \tag{A.34}$$

$$F_V = -ng_v - \frac{D(T)}{T} f_v \tag{A.35}$$

$$g_V = \frac{B}{V(V-B)} \tag{A.36}$$

$$f_V = -\frac{1}{RV(V+B)} \tag{A.37}$$

Michelsen and Hendriks[2] showed, based on the Q function presented before and the chain rule:

$\left(\frac{\partial Q_{SP}}{\partial V}\right) = \left(\frac{\partial Q}{\partial V}\right)_X + \sum_i \sum_{A_i} \frac{\partial Q}{\partial X_{A_i}} \frac{\partial X_{A_i}}{\partial V}$, that the derivative $\left(\frac{\partial Q_{SP}}{\partial V}\right)$ is given by:

$$\left(\frac{\partial Q_{SP}}{\partial V}\right) = \frac{1}{2V}\left(1 - V\frac{\partial \ln g}{\partial V}\right)\sum_i n_i \sum_{A_i}(1 - X_{A_i}) \tag{A.38}$$

Considering equation (A.28), the required derivative $\frac{\partial \ln g}{\partial V}$ for the calculation of the contribution of the association term is given as follow:

$$\frac{\partial g}{\partial V} = -0.475B\left(\frac{1}{V - 0.475B}\right)^2 \tag{A.39}$$

For a Newton – Raphson variant for the calculation of the total volume V, the function that should be minimized is given by equation (A.30) as follows:

$$H(V) = P - \left[\frac{nRT}{V} - \left(\frac{\partial A^r}{\partial V} \right)_{T,n} = \frac{nRT}{V} - \left(\frac{\partial A^r_{SRK}}{\partial V} \right)_{T,n} - \left(\frac{\partial A^r_{association}}{\partial V} \right)_{T,n} \right] \tag{A.40}$$

The derivative is of the function $H(V)$ with respect to volume is also required, meaning that second derivatives of A^r with respect to volume are required. The second derivative can, however, be calculated numerically from equation (A.40); hence an analytical method for estimating the second derivatives is not required.

Literature Sites

(1) Michelsen, M.L.; Mollerup J.M. *Thermodynamic Models: Fundamentals & Computational Aspects.* Tie – line publications: Lyngby, 2004.

(2) Michelsen, M.L.; Hendriks, E.M. Physical properties from association models. *Fluid Phase Equilibria* 2001, 180, 165.

APPENDIX B. Parametarization of CPA EoS

The energy parameter of the CPA equation of state $\alpha(T)$ is given by a Soave-type temperature dependency, while b (hereafter called b_{CPA}) is temperature independent:

$$\alpha(T) = a_o(1 + c_1(1 - \sqrt{T_r}))^2 \tag{B.1}$$

where the reduced temperature is defined in the "conventional" way T/T_c

The CPA model has five pure-compound parameters; three for non-associating compounds (a_0, b_{CPA}, c_1) and two additional parameters for associating compounds ($\varepsilon^{A_iB_j}, \beta^{A_iB_j}$). All pure-compound parameters are typically obtained by fitting experimental vapor pressure and saturated liquid density data. For non-associating compounds e.g. n-alkanes, the three parameters (a_0, b_{CPA}, c_1) can either be obtained from vapor pressures and liquid densities or alternatively via the conventional methodology using critical data and acentric factors.

The above procedure is somewhat inconvenient as it requires knowledge of the experimental critical temperature (T_c) which is used in the calculations. Thus, the exact value of the experimental critical temperature as used in the parameter estimation is required when using CPA together with equation (B.1).

Alternatively, only three "monomer" parameters can be estimated using the conventional SRK expressions:

$$\begin{aligned} \alpha(T) &= \Omega_A \frac{R^2 T_{cm}^2}{P_{cm}} \left[1 + m_m(1 - \sqrt{T/T_{cm}})\right]^2 \\ b &= \Omega_B \frac{RT_{cm}}{P_{cm}} \end{aligned} \tag{B.2}$$

In equation (B.2):

$$\begin{aligned} \Omega_A &= 0.42748 \\ \Omega_B &= 0.08664 \end{aligned} \tag{B.3}$$

i.e. the usual SRK values, but the “critical” parameters and m correspond to the “monomer” and can be calculated from the energy and co-volume parameters of CPA i.e. they are based on optimizing vapor pressures and liquid density data.

By comparing equation (B.2) to the co-volume (b_{CPA}) CPA parameter:

$$b_{CPA} = \Omega_B \frac{RT_{cm}}{P_{cm}} \Rightarrow P_{cm} = \Omega_B \frac{RT_{cm}}{b_{CPA}} \tag{B.4}$$

From equations (B.1) and (B.2) the following expression can be obtained:

$$\begin{gathered}\alpha(T) = a_o(1+c_1(1-\sqrt{T_r}))^2 = \Omega_A \frac{R^2T_{cm}^2}{P_{cm}}\left[1+m_m(1-\sqrt{T/T_{cm}})\right]^2 \Rightarrow \\ \alpha = K_1 - K_2\sqrt{T}\end{gathered} \tag{B.5}$$

where:

$$\begin{gathered}K_1 = (1+c_1)\sqrt{a_0} = (1+m_m)\sqrt{\Omega_A \frac{R^2T_{cm}^2}{P_{cm}}} \\ K_2 = c_1\frac{\sqrt{a_0}}{\sqrt{T_c}} = m_m \frac{\sqrt{\Omega_A \frac{R^2T_{cm}^2}{P_{cm}}}}{\sqrt{T_{cm}}}\end{gathered} \tag{B.6}$$

Combining equations (B.5) and (B.6) the yielding equation for T_{cm} is:

$$\sqrt{T_{cm}} = \frac{(1+c_1)m_m}{c_1(1+m_m)}\sqrt{T_c} \Rightarrow T_{cm} = \frac{\left(\frac{1+c_1}{c_1}\right)^2}{\left(\frac{1+m_m}{m_m}\right)^2}T_c \tag{B.7}$$

Finally by combining equation (B.4) and the K_2 expression of equation (B.6):

$$m_m = c_1 \frac{\sqrt{a_0}\sqrt{T_{cm}}}{\sqrt{T_c}\sqrt{\Omega_A \frac{b_{CPA}RT_{cm}}{\Omega_B}}} \Rightarrow m_m = c_1\sqrt{\frac{a_0\Omega_B}{\Omega_A b_{CPA}RT_c}} \tag{B.8}$$

Using equations (B.4), (B.7) and (B.8) and the CPA parameters (a_0, b_{CPA}, c_1), the “corresponding monomer” parameters can be calculated. This implies that we only need to use the three conventional EoS parameters, the (monomer) critical temperature, pressure and m_m -parameters.

APPENDIX C. ISO 18453 (GERG-water)

DRAFT INTERNATIONAL STANDARD ISO/DIS 18453

ISO/TC **193**/SC **1**	Secretariat: **NEN**
Voting begins on **2002-04-25**	Voting terminates on **2002-09-25**

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Natural gas — Correlation between water content and water dew point

Gaz naturel — Corrélation entre la teneur en eau et le point de rosée de l'eau

ICS 75.060

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Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Introduction

ISO Technical Committee 193 Natural Gas was established in May, 1989, with the task of creating new standards, and updating existing standards relevant to natural gas. This includes gas analysis, direct measurement of properties, quality designation and traceability.

This document provides a reliable mathematical relationship between water content and water dew point in natural gas. The calculation method was developed by GERG; it is applicable in both ways, i.e. to calculate water content or water dew point. Information relating to the thermodynamic principles are given in Annex A; information relating to the traceability, applications and uncertainties associated with this work can be found in the informative Annex B.

Some of the operational problems in the natural gas industry can be traced back to water content in natural gases. Even with a low water vapour content in the gas, changing operating pressure and temperature conditions can cause water to condense and thus lead to corrosion problems, hydrates or ice formation. To avoid this, expensive dehydration units have been installed by natural gas companies. The design and cost of these installations depends on the exact knowledge of the water content at the dew point and the (contractually) required water content.

The instruments resulting from the improvements of moisture measurement equipment during the last decades focus on the determination of water content rather than on water dew point. If therefore the water content is measured, a correlation is needed for expression of water dew point.

The GERG Group identified a need to build a comprehensive and accurate database of measured water content and corresponding water dew point values for a number of representative natural gases in the range of interest before validating the existing correlations between water content and water dew point.

It was subsequently shown that the uncertainty range of the existing correlations could be improved.

Therefore, as a result, a more accurate correlation, composition dependent, was successfully developed on the basis of the new database.

The scope of this document is to standardise the calculation procedure developed by GERG concerning the relationship between water content and water dew point (and vice versa) in the field of natural gas typically for custody transfer.

Note: GERG is an abbreviation of (Groupe Européen de Recherche Gazière).

Natural gas — Correlation between water content and water dew point

1 Scope

To provide the users with a reliable mathematical relationship between water content and water dew point in natura gas when one of the two is known. The calculation method was developed by GERG; it is applicable in both ways i.e. to calculate water content or water dew point.

The document makes no attempt to quantify the measurement uncertainties.

2 Term(s) and definition(s)

For the purposes of this International Standard, the terms and definitions given in ISO/FDIS 14532:2001 "Natural gas - Vocabulary" apply.

In this document the volume measurement is stated under normal reference conditions; the definition given in ISO/FDIS 14532:2001 is: "reference conditions of pressure, temperature and humidity (state of saturation) equal to: 101,325 kPa and 273,15 K for the real, dry gas."

Note 1: The indication of the range of temperature, pressure and composition for which the correlation was validated is given in par. 4.1

Note 2: To clarify, in this document water dew point is the temperature above which no condensation of water (as liquid or as ice) occurs at a specified pressure. In this document gas-hydrates are not considered to be formed.

In addition the following new definitions are given.

Correlation

To bring two or more parameters into a relationship.

Working range

Range of parameters for which the correlation has been validated.

Extended working range

Range of parameters for which the correlation has been developed, but outside the range for which the correlation has been validated.

Uncertainty of the correlation

Absolute deviation of calculated value from the experimental data base.

Note: This does not include any measurement uncertainty in the field.

3 Description

In the past, GERG has identified the necessity for an accurate conversion between the water content and the water dew point for natural gases with sales gas characteristics. To achieve this goal, GERG has defined a research program. In the first phase of the project, reliable data on water content together with data on water dew point were collected for several natural gases for the temperature range of interest: -15 °C to + 5 °C and for the pressure range of interest: 5 bar(a) to 100 bar(a). In addition to the measurements on the seven representative natural gases, measurements were also carried out on the key binary system methane - water. The procedure used for gathering the measured data was the saturation method.

Taking the determined values for the repeatability and reproducibility of the Karl Fischer instrument as consistency criteria for all measured water contents, only a few inconsistent values were detected, which were mainly situated in the range of low water content (high pressure, low temperature range). Values which failed the consistency check were either rejected or - in few cases - weighted much lower in the data pool. In most cases, these values were replaced by repeated measurements carried out at the same pressure and temperature conditions.

Detailed information on the experimental procedure and the composition of the natural gases used during the experiments can be found in the GERG Monograph [1].

The developed relationship is validated for temperatures ranging from -15 °C to +5 °C and pressures ranging from 5 bar(a) to 100 bar(a).

The representative natural gases used for validating the correlation were sampled technically free of glycol, methanol, liquid hydrocarbon and with a maximum content of H_2S of 5 mg/Nm^3. No attempt was made to investigate the impact of the uncertainties resulting from the inclusion of such contaminants.

The thermodynamic background of the developed relationship makes it possible to extend the range of applicability outside the working range to temperatures of -50 °C to +40 °C and pressures from 1 to 300 bar(a) with unknown uncertainties.

It is intended that the correlation be interpreted as reciprocal between water content and water dewpoint; it should be appreciated that this relationship was derived under laboratory conditions using several compositions of natural gas sampled in the field. Under practical field operational conditions significant additional uncertainties are generated.

It must be pointed out that besides the uncertainty in the conversion of the measurement itself, one also has to consider the uncertainties of the measured values; for this purpose ISO CD 15972.1 "Natural gas – Measurement of properties - Single component and condensation properties - Part 1: Water content and water dew point" is relevant.

4 Range of application and uncertainty of the correlation

4.1 Working range

Within the range below the uncertainty is the following:

- for the water dew point calculated from the water content: ± 2°C
- for the water content calculated from the water dew point:
  a) $WC < 580\ \text{mg/Nm}^3$: $0,14 + 0,021 \cdot WC \pm 20$ (mg/Nm^3)
  b) $WC \geq 580\ \text{mg/Nm}^3$: $-18,84 + 0,0537 \cdot WC \pm 20$ (mg/Nm^3)

For the application area, refer to Annex B.

For the application of these formulae, refer to examples given in the Annex C.

Note:

to find the conversion between normal reference conditions and standard reference conditions refer to ISO 13443:1996

- Range of pressure

The range of pressure is $5 \leq p \leq 100$ bar (a)

- Range of temperature

The range of temperature is $-15 \leq t \leq +5$ °C

- Range of composition

The correlation accepts water and the following components as input parameters. The calculation method is applicable for natural gases which meet the limitations listed in the following table (ranges for percentage molar composition):

◆ Methane (CH_4)	$\geq$ 40,0 %
◆ Nitrogen (N_2)	$\leq$ 55,0 %
◆ Carbon dioxide (CO_2)	$\leq$ 30,0 %
◆ Ethane (C_2H_6)	$\leq$ 20,0 %
◆ Propane (C_3H_8)	$\leq$ 4,5 %
◆ 2 – Methyl propane (C_4H_{10})	$\leq$ 1,5 %
◆ n - Butane (C_4H_{10})	$\leq$ 1,5 %
◆ 2,2 – Dimethyl propane (C_5H_{12})	$\leq$ 1,5 %
◆ 2 – Methyl butane (C_5H_{12})	$\leq$ 1,5 %
◆ n - Pentane (C_5H_{12})	$\leq$ 1,5 %
◆ C6+ (Sum of Hexane + higher hydrocarbons) (C_6H_{14})	$\leq$ 1,5 %

Examples of the influence of composition are given in Annex C.

Note: C6+ is treated as n - Hexane

4.2 Extended working range

Extension of the application range may be extrapolated within the following ranges, but the associated uncertainties are unknown.

- Range of pressure

The extended range of pressure is $1 \leq p < 5$ bar (a) and $100 < p \leq 300$ bar (a)

- Range of temperature

The extended range of temperature is $-50 \leq t < -15$ °C and $+5 < t \leq +40$ °C

- Range of composition

The range of components is the same as in 4.1.

5 Correlation

The correlational method is based on the Peng & Robinson equation of state (refer to Annex A for detailed informations).

Note: Annex A provides an extensive overview of the thermodynamic principles of this correlation.

In order to ensure an accurate calculation of water vapour pressure above ice and liquid it was decided to divide the new α function into two parts. In the temperature range 223,15 K to 273,16 K vapour pressure data above ice, in the temperature range 273,16 K to 313,15 K vapour pressure data over liquid water was used to define the α function.

$$\alpha(T_R)^{1/2} = 1 + A_1 \cdot \left(1 - T_R^{\ 1/2}\right) + A_2 \cdot \left(1 - T_R^{\ 1/2}\right)^2 + A_3 \cdot \left(1 - T_R^{\ 1/2}\right)^4$$

Below is given the list of the coefficients of the new α function.

FOR $\Rightarrow$ 223,15 K $\leq$ T < 273,16 K

A_1 = 0,106025

A_2 = 2,683845

A_3 = -4,75638

FOR $\Rightarrow$ 273,16 K $\leq$ T < 313,15 K

A_1 = 0,905436

A_2 = -0,213781

A_3 = 0,26005

A reliable estimate for the parameter was obtained from an appropriate set of vapour-liquid equilibria data.

The optimum parameters for binary parameters k_{ij} are found by satisfying a specified statistical criterion (minimization of an objective function through a least squares fit algorithm). For the binary systems carbon dioxide/water, methane/water and ethane/water, it was necessary to introduce temperature dependent interaction parameters to get a satisfactory description of the vapour-liquid equilibrium. The temperature dependence is given as:

$$k_{ij}(T) = k_{ij,0} + k_{ij,1} \cdot \left(\frac{T}{273{,}15} - 1\right)$$

This definition of $k_{ij}(T)$ has the advantage that k_{ij} equals $k_{ij,0}$ when the temperature equals 0 °C. The parameters of the binary water system are optimised for the extended working range of this correlation (-50°C up to 40 °C). Extrapolation of the data beyond the extended working range is not allowed.

Indicated below are:

- Pure component data
- Overview over the complete binary interaction parameters.

Pure component data (compound properties used in the calculation)

Component	ω	Pc	Tc	Source
◆ Water (H_2O)	0.34437	220.64	647.14	Knapp (1982) [11]
◆ Nitrogen (N_2)	0.03593	33.99	126.26	Knapp (1982) [11]
◆ Carbon dioxide (CO_2)	0.22394	73.86	304.21	Knapp (1982) [11]
◆ Methane (CH_4)	0.0114	45.99	190.55	Knapp (1982) [11]
◆ Ethane (C_2H_6)	0.09909	48.72	305.33	Knapp (1982) [11]
◆ Propane (C_3H_8)	0.15611	42.46	369.85	Knapp (1982) [11]
◆ 2 – Methyl propane (i-C_4H_{10})	0.18465	36.4	407.85	Knapp (1982) [11]
◆ n – Butane (n-C_4H_{10})	0.19777	37.84	425.14	Knapp (1982) [11]
◆ 2,2 – Dimethyl propane (neo-C_5H_{12})	0.19528	31.96	433.75	Knapp (1982) [11]
◆ 2 – Methyl butane (i-C_5H_{12})	0.22606	33.7	460.39	Knapp (1982) [11]
◆ n – Pentane (n-C_5H_{12})	0.24983	33.64	469.69	Knapp (1982) [11]
◆ n – Hexane (C_6H_{14})	0.296	30.2	507.85	Knapp (1982) [11]

ω ⇒ acentric factor

Pc ⇒ critical pressure, bar

Tc ⇒ critical temperature, K

Binary Interaction Parameters are the following:

Component(i)	Component(j)	$k_{ij,0}$	$k_{ij,1}$	Source	
Water	Nitrogen	0.4800	0	GERG	[1]
Water	Carbon dioxide	0.184	0.236	GERG	[1]
Water	Methane	0.651	-1.385	GERG	[1]
Water	Ethane	0.635	-0.93	GERG	[1]
Water	Propane	0.53	0	GERG	[1]
Water	n - Butane	0.69	0	GERG	[1]
Water	n - Pentane	0.5	0	GERG	[1]
Water	n - Hexane	0.5	0	GERG	[1]
Water	2 – Methyl propane	0.69	0	GERG	[1]
Water	2,2 Dimethyl propane	0.5	0	GERG	[1]
Water	2 – Methyl butane	0.5	0	GERG	[1]
Nitrogen	Carbon dioxide	-0.0170	0	Knapp(1982)	[8]
Nitrogen	Methane	0.0311	0	Knapp(1982)	[8]
Nitrogen	Ethane	0.0515	0	Knapp(1982)	[8]
Nitrogen	Propane	0.0852	0	Knapp(1982)	[8]
Nitrogen	n - Butane	0.0800	0	Knapp(1982)	[8]
Nitrogen	n - Pentane	0.1000	0	Knapp(1982)	[8]
Nitrogen	n - Hexane	0.1496	0	Knapp(1982)	[8]
Nitrogen	2 – Methyl propane	0.1033	0	Knapp(1982)	[8]
Nitrogen	2,2 Dimethyl propane	0.0930	0	Avlonitis (1994)	[7]
Nitrogen	2 – Methyl butane	0.0922	0	Knapp(1982)	[8]
Carbon dioxide	Methane	0.0919	0	Knapp(1982)	[8]
Carbon dioxide	Ethane	0.1322	0	Knapp(1982)	[8]
Carbon dioxide	Propane	0.1241	0	Knapp(1982)	[8]
Carbon dioxide	n - Butane	0.1333	0	Knapp(1982)	[8]
Carbon dioxide	n - Pentane	0.1222	0	Knapp(1982)	[8]
Carbon dioxide	n - Hexane	0.1100	0	Knapp(1982)	[8]
Carbon dioxide	2 – Methyl propane	0.1200	0	Knapp(1982)	[8]
Carbon dioxide	2,2 Dimethyl propane	0.1260	0	Kordas (1994)	[9]
Carbon dioxide	2 – Methyl butane	0.1219	0	Knapp(1982)	[8]
Methane	Ethane	-0.0026	0	Knapp(1982)	[8]
Methane	Propane	0.0140	0	Knapp(1982)	[8]
Methane	n - Butane	0.0133	0	Knapp(1982)	[8]
Methane	n - Pentane	0.0230	0	Knapp(1982)	[8]
Methane	n - Hexane	0.0422	0	Knapp(1982)	[8]
Methane	2 – Methyl propane	0.0256	0	Knapp(1982)	[8]

Methane	2,2 Dimethyl propane	0.0180	0	Kordas (1995)	[10]
Methane	2 – Methyl butane	-0.0056	0	Knapp(1982)	[8]

Component(i)	Component(j)	$k_{ij,0}$	$k_{ij,1}$	Source	
Ethane	Propane	0.0011	0	Knapp(1982)	[8]
Ethane	n - Butane	0.0096	0	Knapp(1982)	[8]
Ethane	n - Pentane	0.0078	0	Knapp(1982)	[8]
Ethane	n - Hexane	-0.0100	0	Knapp(1982)	[8]
Ethane	2 – Methyl propane	-0.0067	0	Knapp(1982)	[8]
Ethane	2,2 Dimethyl propane	0.0230	0	Nishiumi (1988)	[6]
Ethane	2 – Methyl butane	0.0160	0	Nishiumi (1988)	[6]
Propane	n - Butane	0.0033	0	Knapp(1982)	[8]
Propane	n - Pentane	0.0267	0	Knapp(1982)	[8]
Propane	n - Hexane	0.0007	0	GERG	[1]
Propane	2 – Methyl propane	-0.0078	0	Knapp(1982)	[8]
Propane	2,2 Dimethyl propane	0	0		
Propane	2 – Methyl butane	0.0111	0	Knapp(1982)	[8]
2 – Methyl propane	n - Butane	-0.0004	0	GERG	[1]
2 – Methyl propane	n - Pentane	0	0		
2 – Methyl propane	n - Hexane	0	0		
2 – Methyl propane	2,2 Dimethyl propane	0	0		
2 – Methyl propane	2 – Methyl butane	0	0		
n - Butane	n - Pentane	0.0174	0	Knapp(1982)	[8]
n - Butane	n - Hexane	-0.0056	0	K-BP^2	[11]
n - Butane	2,2 Dimethyl propane	0	0		
n - Butane	2 – Methyl butane	0	0		
2,2 Dimethyl propane	2 – Methyl butane	0	0		
2,2 Dimethyl propane	n - Pentane	0	0		
2,2 Dimethyl propane	n - Hexane	0	0		
2 – Methyl butane	n - Pentane	0.060	0	Knapp(1982)	[8]
2 – Methyl butane	n - Hexane	0	0		
n - Pentane	n - Hexane	0	0		

APPENDIX D. List of Publications

Parts of this work are published in the following manuscripts:

Folas, G.K.; Frøyna, E.W.; Løvland, J.; Kontogeorgis, G.M.; Michelsen, M.L.; Solbraa, E. Data and prediction of water content of high pressure nitrogen, methane and natural gas. *Accepted for publication to Fluid Phase Equilibria.*

Folas, G.K.; Kontogeorgis, G.M.; Michelsen, M.L.; Stenby, E.H. Vapor – Liquid, Liquid – Liquid and Vapor – Liquid – Liquid equilibrium of binary and multicomponent systems with MEG. Modeling with the CPA EoS and an EoS/G^E model. *Fluid Phase Equilibria* **2006,** *249,* 67-74.

Kontogeorgis G.M.; Michelsen M.L.; Folas G.K.; Derawi, S.O.; von Solms, N.; Stenby E.H. Ten years with the CPA (Cubic-Plus-Association) equation of state. Part I. Pure compounds and Self-associating systems. *Ind. Eng. Chem. Res.* ***2006,*** 45, 4855-4868.

Kontogeorgis G.M.; Michelsen M.L.; Folas G.K.; Derawi, S.O.; von Solms, N.; Stenby E.H. Ten years with the CPA (Cubic-Plus-Association) equation of state. Part II. Cross-associating and multicomponent systems. *Ind. Eng. Chem. Res.* ***2006,*** 45, 4869-4878.

Folas, G.K.; Kontogeorgis, G.M.; Michelsen, M.L.; Stenby, E.H. Application of the cubic – plus – association (CPA) equation of state to mixtures with polar chemicals and high pressures. *Ind. Eng. Chem. Res.* **2006**, 45, 1516 – 1526.

Folas G.K.; Michelsen M.L.; Stenby E.H.; Kontogeorgis G.M.; Solbraa, E. Liquid-liquid equilibria for binary and ternary systems containing glycols, aromatic hydrocarbons, and water: Experimental measurements and modeling with the CPA EoS, *J. Chem. Eng. Data* ***2006,*** 51, 977 – 983.

Folas, G.K.; Kontogeorgis, G.M.; Michelsen, M.L.; Stenby, E.H. Application of the cubic – plus – association (CPA) equation of state to complex mixtures with aromatic hydrocarbons. *Ind. Eng. Chem. Res.* **2006**, 45, 1527 – 1538.

Folas, G.K.; Gabrielsen, J.; Michelsen, M.L.; Stenby, E.H.; Kontogeorgis, G.M. Application of cubic - plus – association (CPA) Equation of State to cross – associating systems. *Ind. Eng. Chem. Res.* **2005,** *44,* 3823.

Folas, G.K.; Derawi, S.O.; Michelsen, M.L.; Stenby, E.H.; Kontogeorgis, G.M. Recent applications of the Cubic – Plus – Association (CPA) equation of state to industrially important systems. *Fluid Phase Equilibria* **2005,** *228-229,* 121.