Extended abstract summary

Summary

The purpose of this PhD work was to extend the Cubic-Plus-Association (CPA) equation of state (EoS) to electrolytes and thus be able to handle simultaneously polar/associating compounds, hydrocarbons and a variety of ions from fully dissociated salts. The ultimate goal was to develop a theoretically-oriented model which can handle a wide variety of mixtures and properties in an as predictive way as possible.

The CPA EoS has during the past 20 year been applied to thermodynamic modeling of a wide range of industrially important chemicals, mainly in relation to the oil- and gas sector. One of the strengths of the CPA EoS is that it reduces to the Soave Redlich Kwong (SRK) cubic EoS in the absence of associating compounds and is therefore compatible with existing tools for oil characterization. In a similar fashion, the electrolyte CPA (e-CPA) EoS should reduce to the CPA EoS in the absence of electrolytes, making it possible to extend the applicability of the CPA EoS while retaining backwards compatibility and resuing the parameters for non-electrolyte systems.

There are many challenges related to thermodynamic modeling of mixtures containing electrolytes, and many different approaches to the development of an electrolyte EoS have been suggested by scientists in the field. However, most of these approaches are focusing on aqueous solutions and cannot easily be extended to handle mixed solvents. Furthermore, the approaches suggested in current literature have rarely been applied to all types of thermodynamic equilibrium calculations relevant to electrolyte solutions.

This project has aimed to determine the best recipe to deliver a complete thermodynamic model capable of handling electrolytes in mixed solvents and at a wide range of temperature and pressure. Different terms describing the electrostatic interactions have been compared and it was concluded that the differences between the Debye-Hückel and the "mean spherical approximation" models are negligible. A term accounting for the Gibbs energy of hydration (such as the Born term) must be included in order to provide sufficient driving forces for electrolytes towards the most polar phase.

The static permittivity of the mixture was found to be the most important property; yet it was shown that the empirical models suggested by literature could lead to unphysical behavior of the equation of state. A new theoretical model was developed to extend the framework for modeling of the static permittivity to hydrogen-bonding compounds and salts. The model relates the geometrical configuration of hydrogen-bonding dipolar molecules to the Kirkwood g-factor using the Wertheim association model that is included with modern EoS such as CPA or SAFT (Statistical Associating Fluid Theory). This new model was shown to give excellent predictions of the static permittivity of mixtures over wide ranges of temperature, pressure, and composition and thereby generalizes the handling of electrolytes in mixed solvents in an electrolyte EoS.

The CPA EoS was extended with a Debye-Hückel and a Born term to account for the electrostatics along with the new model for the static permittivity. This new e-CPA EoS was parameterized against osmotic coefficient, density, and mean ionic activity coefficient data of pure salts and validated against salt mixture data. The model was then applied to predict:
• the solubility of light gases, hydrocarbons, and aromatics in aqueous mixtures and mixed solvents
• solid-liquid equilibrium in aqueous salt mixtures and mixed solvents

• gas hydrate formation pressures of methane with salts in water+methanol
• liquid-liquid and liquid-liquid-liquid equilibrium with water-propan-1-ol-NaCl-octane solutions
It was demonstrated that the model has a good potential for applications in relation to e.g. flow assurance during the production of natural gas. The parameterization of electrolyte EoS is of high importance and more work is needed in order to obtain good ion-specific parameters that include interaction parameters with gases and relevant chemicals.

Problem addressed and state of the art

The Cubic-Plus-Association (CPA) equation of state (EoS) has been successfully applied in modeling of the phase equilibrium of natural gas components in mixtures of water, glycols or alcohols [1]. The purpose of this work was to extend CPA to account for the presence of ions using some of the following contributions to the Helmholtz energy:
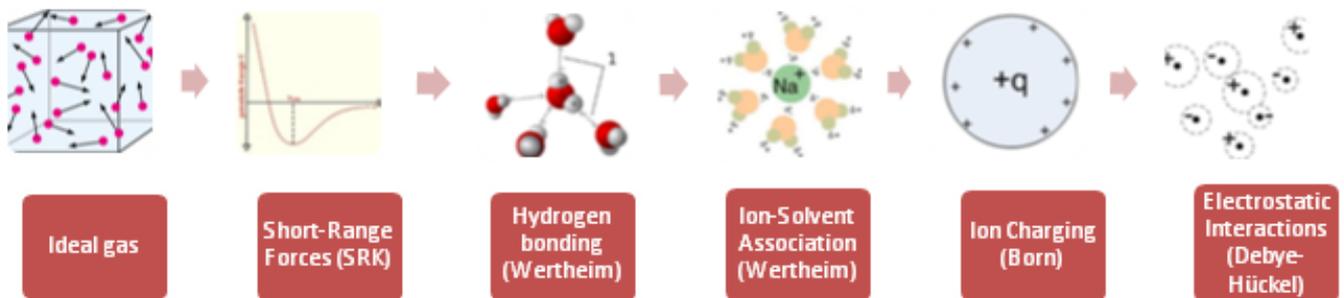
It is clear from this illustration that several factors are unclear when extending the CPA or any equation of state to mixtures containing electrolytes:

Which and how many electrolyte terms should be included ?

How i.e. by which theory should the electrostatic interactions be described ? (Debye-Huckel, MSA, other?)

1. Do we need a Born-type term for the charging of ions ?
2. Do we need an ion-solvent association term ?
3. Should we approach the problem from the "primitive" point of view (solvent is a continuum) or from the more complex molecular approach where all interactions should be accounted for ?
4. If continuum, how can we estimate the dielectric constant in a reliable way and is this really required?
5. Last but not least, how can we estimate the model parameters in a way that makes sense and can render the model suitable for a wide range of practical applications –and if possible in a predictive way ?

These are only some of the key questions when developing electrolyte equations of state and thus it is no big surprise that a very wide and differently developed e-EoS have been proposed. These are summarized and critically compared in the first chapter of the thesis (section 1.6, esp. tables 1.2 and 1.3). This analysis

showed that, unfortunately, essentially none of the above questions have been answered in a satisfactory matter and the PhD thesis addresses several of them.

It has been early in the thesis work decided to focus on the "primitive" approach as non-primitive engineering oriented approaches were not felt to be within the time horizon of a single PhD, but all the other questions were addressed in this work.

The key discoveries – innovations are presented in the next section, while detailed results and applications are presented next.

Key innovations

1. Debye-Huckel vs. MSA

The first innovation is the significant understanding of different models for electrostatic interactions, especially the MSA (mean spherical approximation) and the Debye-Hückel theories.
This was an important task to undertake, as it is often reported that MSA is a superior model, possibly because of its theoretical origin (derivation from statistical thermodynamics). Thus, the validity of the conclusions from various research groups regarding the use of MSA vs. Debye-Hückel should be checked.
Bjørn Maribo-Mogensen has both derived fully and implemented himself both models (including the full version of MSA).
The major conclusion from this work is that MSA and the Debye-Hückel models were found to perform similarly (in terms of the reduced Helmholtz energy) if the Debye-Hückel distance of closest approach parameter was set to 5/6 of the MSA diameter. This work is published in the open literature [article 1 above, also attached, ref.2].
It was shown in the same work [2] that the dielectric constant is the most important parameter which influences the electrostatic interactions. It was shown that the dielectric constant and its concentration dependency are actually a much more important parameter than selecting MSA or DH for the electrostatic interactions. It was also shown that using an empirical model for the dielectric constant may introduce possible unphysical behavior into the equation of state, which can greatly influence equilibrium properties.

2. Predictive model for the dielectric constant

These observations [under point 1, from ref.2] were the starting step for Bjørn for developing a theoretically sound model for predicting the dielectric properties of complex fluids. This was considered necessary as the existing models for dielectric constants of mixtures are empirical and only support aqueous solutions. To improve the reliability of the thermodynamic model, a new predictive model for the dielectric constant and refractive index of mixtures has been developed based on the theory of dipole fluctuations by Onsager, Kirkwood and Fröhlich, using a geometrical model for the hydrogen-bond networks. The model is capable of predicting the static permittivity of pure compounds and complex mixtures over wide temperature and pressure ranges. Bjørn was able with his model to predict the static permittivity for a very wide range of systems, from pure compounds (water, alcohols, glycols) are a function of temperature, binary water-alcohol and water-glycol mixtures over the whole concentration range and an extensive temperature-range as well as

both low and high pressures, and finally his model has be used for predictions for ternary mixtures e.g. of water-ethylene glycol-methanol.

In contrast to the empirical models that are often included in electrolyte models, the new model for predicting the static permittivity of complex mixtures has the correct physical behavior, which is important when the model is used in the context of equations of state.

It is also possible to determine the complex (frequency-dependent) permittivity using a relaxation model. The results are excellent illustrating that a very successful theoretically sound model for the static permittivity has been developed, also for salt containing mixtures. This work has been published in two articles in *Journal of Physical Chemistry B*. [3,4].

3. *The importance of the Born term*

Bjørn's work has also illustrated the importance of the Born term for solvation and that such a term should be included in an equation of state.

4. *Development and parameterization of the electrolyte CPA equation of state*

Bjørn has himself programmed a full version of an electrolyte equation of state based on CPA. His e-CPA model includes the CPA model for physical and association interactions as well as the DH and Born terms. Using a simple parameterization approach, the developed e-CPA is capable of correlating the density, the activity-, and the osmotic coefficients of the NaCl-water and other aqueous salt systems over wide temperature ranges, when including ion association. He proved that ion association effects are important. A full parameterization of the model has been recently completed and an article has been submitted to *AIChE J.* [5] (special issue in honour of John M. Prausnitz).

Very satisfactory results are obtained, besides activity coefficients, for calculation of salting-out and gas hydrate formation curves.

Applications, implementations and results

Some more details on the above mentioned innovations and some results are shown below.

Thermodynamics of Electrostatic Interactions

The theoretical foundations of electrolyte thermodynamics have been laid forth by many of the 18th, 19th, and 20th century's most distinguished scientists. C. A. de Coulomb published in 1785 the fundamental result for the force between two charged spheres as a function of the inverse-square distance r. Debye and Hückel (DH) [6] solved the Poisson equation assuming that the charges surrounding a central ion followed a Boltzmann distribution. They determined the electrical potential ψ_i from Eq. (1) [2]:

$$\psi_i\left(r,\lambda\right) = \frac{\lambda q_i}{4\pi\varepsilon_0\varepsilon_r r} - \frac{\lambda q_i}{4\pi\varepsilon_0\varepsilon_r}\frac{\lambda\kappa}{1+\lambda\kappa d_i} \qquad r \leq d_i \qquad\qquad (1)$$

The electrostatic energy can then be determined through the partial charging procedure from Eq. (2):

$$A^{el} = \sum_i n_i q_i \int_0^1 \psi_i(r, \lambda) d\lambda = -\frac{N_A e^2}{4\pi\varepsilon_0 \varepsilon_r} \sum_i^N \frac{n_i z_i^2}{d_i} \left[\frac{\ln(1 + \kappa d_i) - \kappa d_i}{(\kappa d_i)^2} + \frac{1}{2} - \beta \right] \qquad (2)$$

Using $r = d_i$ gives the DH solution where $\beta = 0$. Using $r = \frac{1}{2} d_i$ gives the DH + Born term with $\beta = 1$. Eq. (3) shows the Born energy of transfer [6] at infinite dilution from vacuum to liquid calculated from Eq. (2).

$$\lim_{n_i=0} \left(\mu_i^{(l)} - \mu_i^{(v)} \right) = \beta \frac{N_A e^2}{4\pi\varepsilon_0} \frac{z_i^2}{d_i} \left(\frac{1}{\varepsilon_r} - 1 \right) = \beta \Delta A_{Born} \qquad (3)$$

Figure 1 shows a comparison of the chemical potential from a CPA EoS. Eq. (3) provides the dominating driving force for keeping the ions in the polar phase; making it crucial for oil-water equilibrium [7,8].
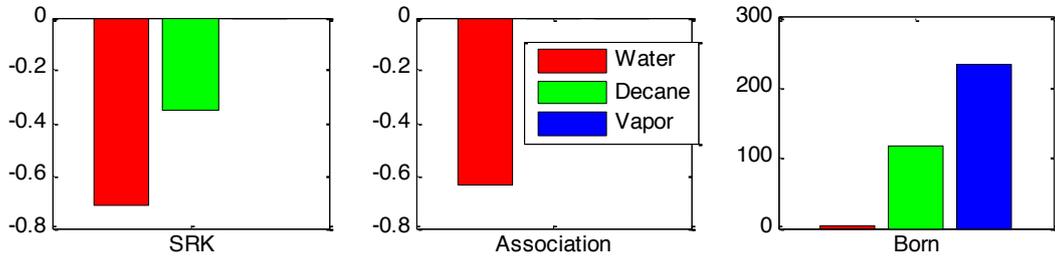

Figure 1: Chemical potential (1/RT $\partial A/\partial n$) of Na$^+$ at infinite dilution from different terms in the oil, water, and vapor phase.

Debye-Hückel vs. MSA

The DH equation has often been confused with the limiting law arising from a first-order Taylor expansion of Eq. (2) which is only valid at low concentrations [2]. This has incorrectly led to the conclusion that the DH equation in Eq. (2) is not suited for high concentrations, and several authors have argued for the use of the mean spherical approximation (MSA) derived from statistical mechanics by L. Blum [9]. Bjørn showed [2] that there are negligible differences between the full (implicit) MSA and the full DH equation even in concentrated solutions, and that the results were much more sensitive to the model used for the static permittivity than to the use of either MSA or DH. The main results are summarized in Figure 2:
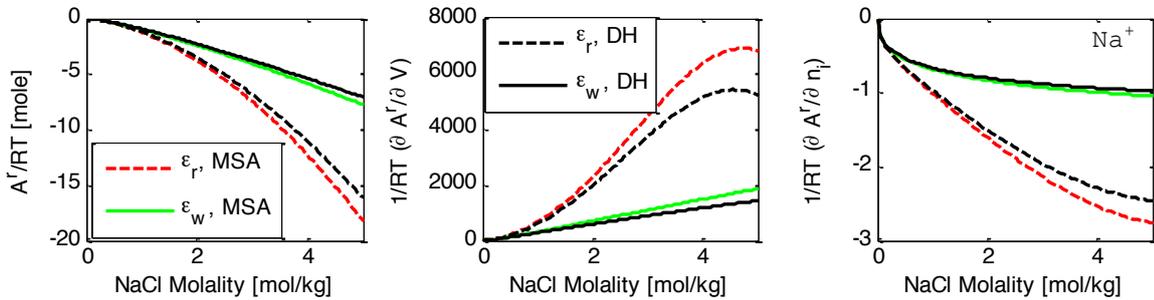

Figure 2: Comparison of the Helmholtz energy when including effect of ions on permittivity (ε_r) and a permittivity equal to water (ε_w). Empirical model for salt effect may introduce non-physical behavior (e.g. additional volume roots).

How to calculate the static permittivity?

Despite the importance of the static permittivity there is no consensus among researchers; should we use ε_r of the pure or mixed solvent [10-21]?, should we account for ion effect through empirical models [22-26]? Or should we use non-primitive models where the static permittivity is calculated implicitly within the equation of state itself from dipole-dipole, ion-dipole, and ion-ion interactions [27,28]? To answer this important question Bjørn developed a new predictive model for the static permittivity of fluid mixtures containing both non-polar, polar, hydrogen-bonding compounds [3] and ions [4]. The theory of dipolar fluctuations [29,30] was extended with a geometric model for dipolar correlations in a hydrogen-bond network to account for dipolar correlations. The static permittivity ε_r is calculated using Eq. (4):

$$\frac{\left(2\varepsilon_r + \varepsilon_\infty\right)\left(\varepsilon_r - \varepsilon_\infty\right)}{\varepsilon_r} = \left(\frac{\varepsilon_\infty + 2}{3}\right)^2 \frac{N_A \rho}{\varepsilon_0 k_B T} \sum_i x_i X_i g_i \mu_{i,0}^2 \qquad g_i = 1 + \sum_j \frac{z_{ij} P_{ij} \cos\gamma_{ij}}{P_i \cos\theta_{ij} + 1} \frac{\mu_{0,j}}{\mu_{0,i}} \qquad (4)$$

Where ε_∞ is approximated by the squared refractive index n^2 calculated from the Clausius-Mossotti equation, $\mu_{i,0}$ is the vacuum dipole moment, ρ the molar density calculated from CPA, x_i mole fraction i, X_i the fraction of i that is not bound to an ion (assuming dipoles in the electrical field from the ion does not contribute to overall dipole moment density [4]), g_i is the Kirkwood g-factor for dipolar correlations calculated from the coordination number z_{ij} and angles γ_{ij} and θ_{ij}. The probabilities of association between molecule i and j P_{ij} as well as probability of association of component I $P_i = \sum P_{ij}$ are both calculated within the CPA equation of state using the Wertheim association framework [1]. Based on correlation of θ_i for the pure components only, the model gives excellent predictions for binary and ternary mixtures over wide temperature and pressure ranges as shown in Figure 3.
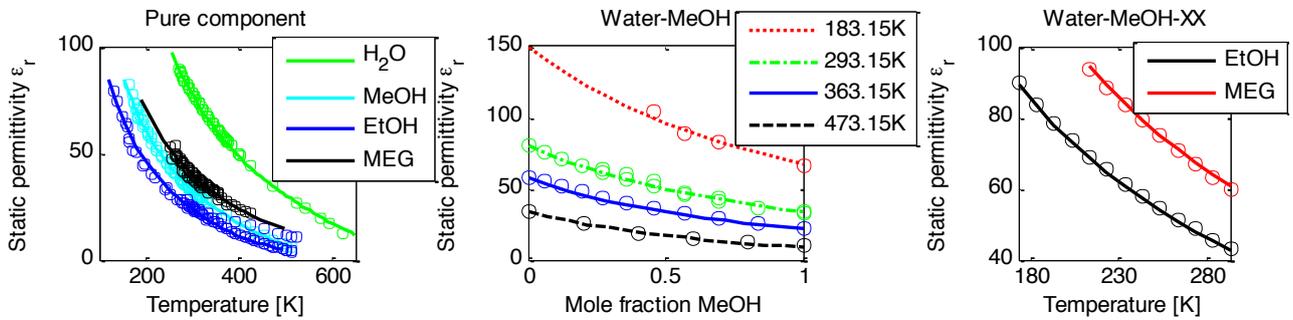

Figure 3: Correlated static permittivity calc. with CPA (left) [4]. Predicted static permittivity of methanol-water (middle, colored at 1 bar, black at 100 bar) [26]. Predictions for the ternary mixtures (right) of water (50vol%), methanol (25vol%), ethylene glycol (25vol%) [4], and of water (20vol%), methanol (55vol%), ethanol (25vol%) [27]. Data from Landolt-Börnstein [31].

The presence of salts reduces the static permittivity primarily through the mechanism of dielectric saturation, where solvent molecules are directed by the electrical field. Bjørn included this effect through ion-solvent association using the Wertheim association framework where each ion is assumed to have ϕ_j identical association sites. Bjørn calculated the ion-solvent cross-association strength β_{ij} from the solvation number at infinite dilution N_{ij}, and either fit the cross-association energy ε_{ij} to experimental data or use the mCR-1 (solvation) combining rule $\varepsilon_{ij}=0.5\varepsilon_i$ [4]. Figure 4 was obtained using the solvation numbers below:

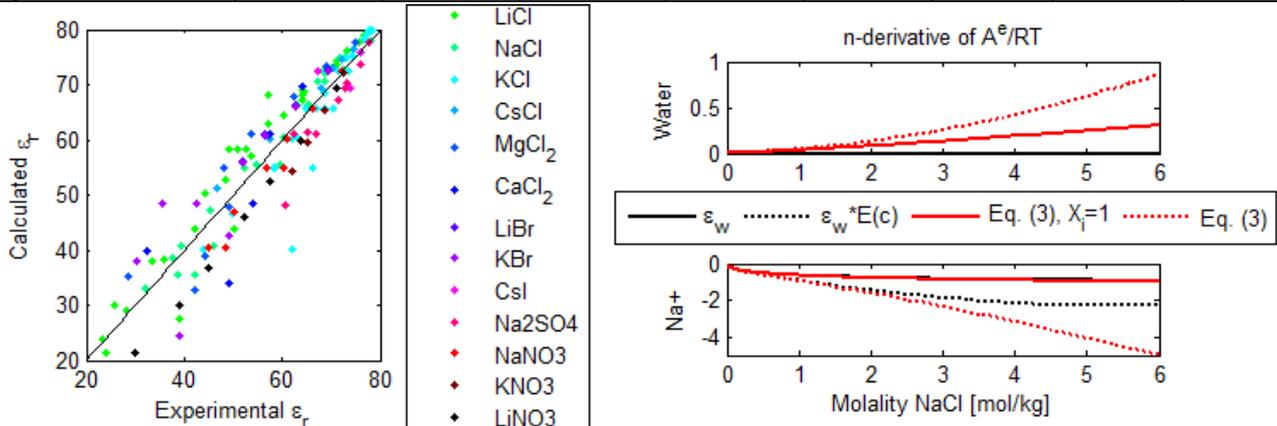| Ion	Na^+	K^+	Ca^{+2}	Cl^-	Br^-	I^-	NO_3^-	SO_4^{-2}
Hydration number	6	6	8	5	5	5	5	5

Figure 4: Correspondence of dielectric constant data (left). Derivatives of Debye-Hückel model with new model (right). [4]

Figure 4 (left) shows good correspondence with the static permittivity of water-salt solutions reported in literature. Figure 4 (right) shows a comparison of compositional derivatives of Debye-Hückel with the new model (red) and the empirical correlations used in [2], with (dashed) an without (solid) account for the effect of ions. It shows that the new model has a dramatic effect on the constant-volume/temperature chemical potential from Debye-Hückel, and that it now provides a significant contribution to the water activity, reflecting the physical effect that adding more dipolar molecules to a fixed volume containing water and ions will increase the static permittivity. The new model also drastically affects derivatives wrt. T and V. Such effect cannot be captured through the empirical models commonly adopted in literature [2,4].

In practice results for the static permittivity of salt-water solutions are scattered, scarce, often inconsistent and are subject to systematic errors [4]. The most severe error arises from the electrophoretic effect discovered by Hubbard and Onsager [32-35] causing a reduction in the measured permittivity in an electrical field due to the movement of ions in the order of 25-75%. It must not be used for thermodynamic modeling as it is a dynamic effect [4,32-37], but as the extent of the effect cannot be determined accurately, the effect has been ignored by previous groups working within electrolyte thermodynamics.

The final phase of the project is summarized in the most recent publication [4] where a complete electrolyte CPA equation of state is presented. While the details are presented in this article, figures 5-10 show some typical results. Very few adjustable parameters are used and they are fitted to activity and osmotic coefficients. It is shown that e-CPA can correlate such activity coefficients quite well over extensive temperature ranges, while it can also predict solid-liquid equilibria (mixed salts), gas solubilities, salt solubility in mixed solvents and gas hydrate curves, among much more. The model has been widely applied and thus the predictive capabilities of the new EoS will be assessed for important flow assurance properties, including freezing point depression, salting out, gas hydrate inhibition, and scaling in mixed solvents. The model will also be made available in commercial process simulators, such as Aspen HYSYS through a CAPE-OPEN library in C# developed during the PhD [38].
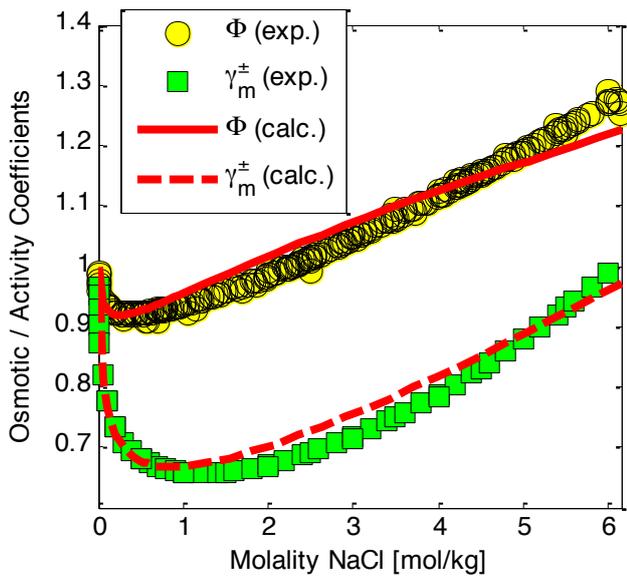
Figure 5: Correlated with e-CPA osmotic coefficients and activity coefficients for NaCl at 25°C.
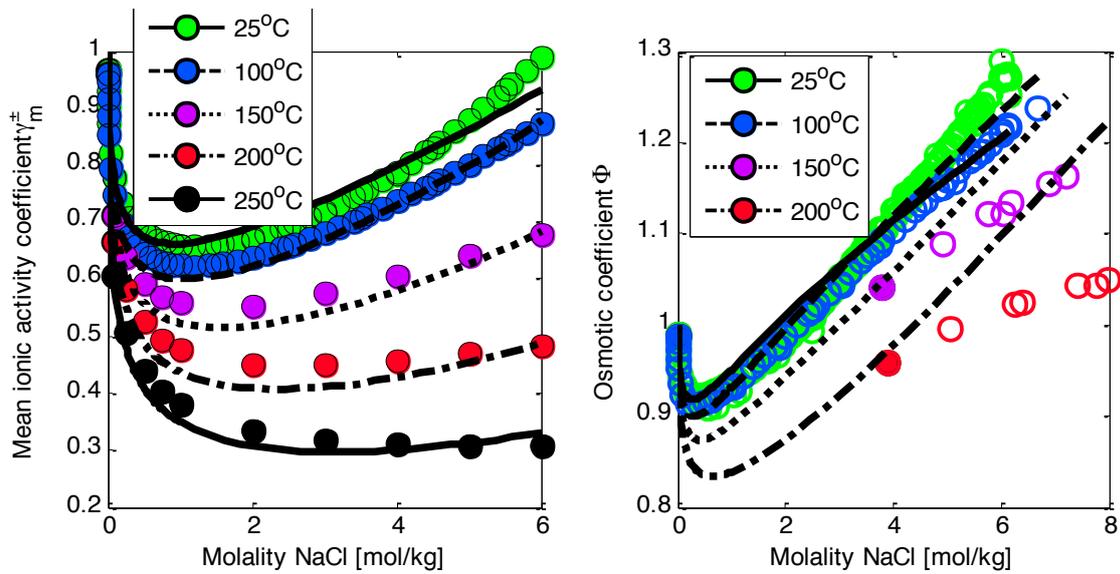

Figure 6: Results with e-CPA. Temperature and concentration dependence of NaCl activity coefficients (left) and osmotic coefficients (right) compared to experimental data.
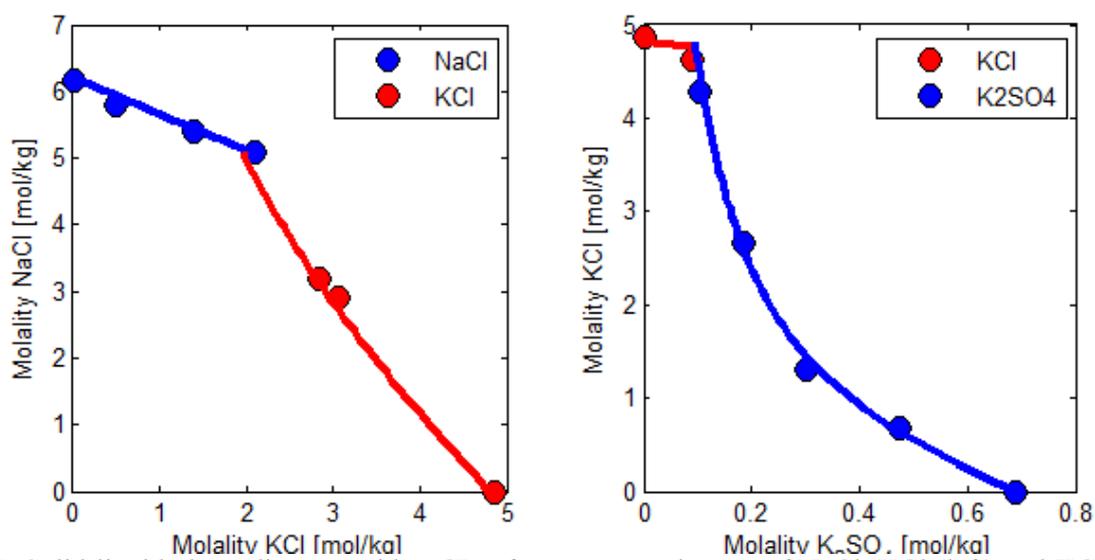
Figure 7: Solid-liquid phase diagram with e-CPA for aqueous mixtures of NaCl+KCl (left) and KCl+K$_2$SO$_4$ (right) at 25°C.
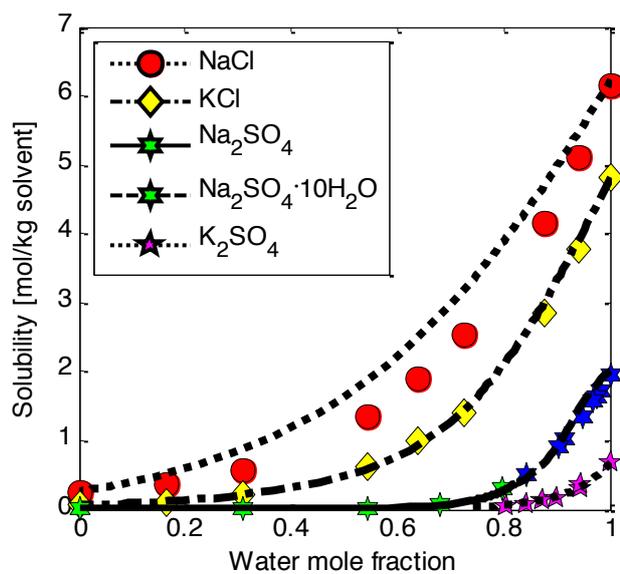

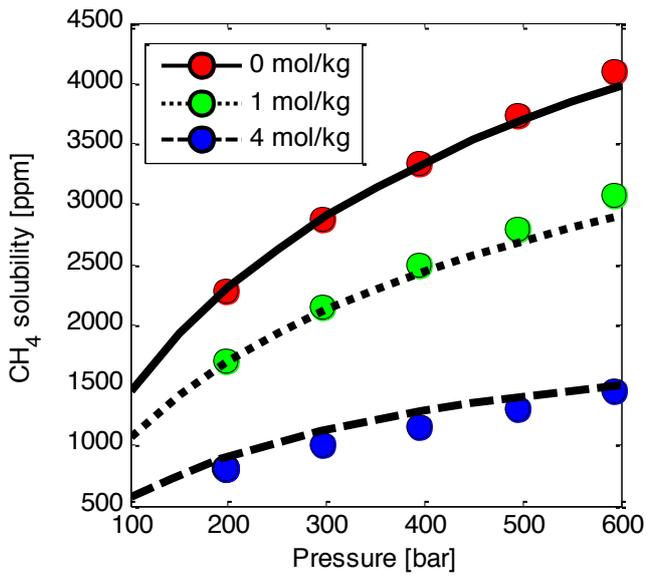Figure 8: Solubility of different salts in water + methanol with e-CPA.

Figure 9: Solubility of methane in water with NaCl at 51.5°C using e-CPA against experimental data from O'Sullivan and Smith (1970).
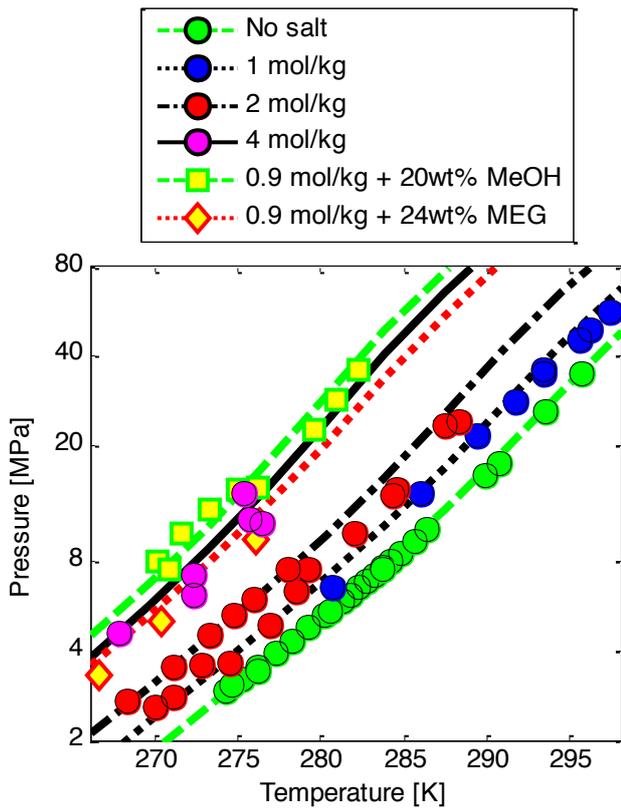

Figure 10: Predicted with e-CPA effect of NaCl on the gas hydrate formation pressure in pure water and mixtures with methanol and ethylene glycol. Data was obtained from the NIST (2014) Clathrate Hydrate Database. Note that the pressure scale is logarithmic.

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