The Debye-Hückel theory and its importance in modeling electrolyte solutions

A colleague at the Technical University of Denmark has often stated: "Life is too short for electrolytes". Another well-known scientist in the field of molecular simulation has recently said during an international Thermodynamics conference: "All my life I have tried to keep myself away from water and electrolytes". Sadly, what these statements correctly imply is that there are far too many unclear questions and concepts in electrolyte thermodynamics, and associated difficulties in modeling electrolyte solutions. In this work, we attempt to shed some light on some important concepts and misconceptions in electrolyte thermodynamics associated with the development of electrolyte equations of state, with emphasis on those based on the Debye-Hückel theory. Detailed mathematics is needed for some of the derivations but for brevity and in order to emphasize the principles rather than the derivations, the latter are omitted. We first discuss the peculiarities of electrolyte thermodynamics and associated modeling and continue with the derivation of the Debye-Hückel theory. The assumptions and limits of application of Debye-Hückel are discussed in particular. Next, the Born term and its significance and implications are presented in more detail. A discussion and outlook section conclude this review. Several of the statements in this work challenge “accepted beliefs” in electrolyte thermodynamics and, while we believe that this challenge is justified, we hope that a useful debate can result in improved and predictive thermodynamic models for electrolyte solutions.

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A collocation method for surface tension calculations with the density gradient theory
Surface tension calculations are important in many industrial applications and over a wide range of temperatures, pressures and compositions. Empirical parachor methods are not suitable over a wide condition range and the combined use of density gradient theory with equations of state has been proposed in literature. Often, many millions of calculations are required in the gradient theory methods, which is computationally very intensive. In this work, we have developed an algorithm to calculate surface tensions an order of magnitude faster than the existing methods, with no loss of accuracy. The new method can be used with any equation of state, and gives much improved performance. In this work, the new method for solving the gradient density theory equations is combined with cubic equations of state and the Cubic-Plus-Association model. Applications for both binary and multicomponent mixtures and for both hydrocarbon and associating systems are shown. For most systems, the predictions obtained are in good agreement with experimental data. However, cases have been identified where further investigation is needed.

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A comment on water’s structure using monomer fraction data and theories

Monomer fraction data for water (and other compounds) can provide useful information about their structure and can be used in “advanced” equations of state, which account explicitly for association phenomena. Recent findings about the performance of association theories in representing the monomer fraction of water are reviewed. Three such theories are considered and all of them perform qualitatively similar. They can all represent phase equilibria for water solutions qualitatively well but with parameters which are not in good agreement with Luck’s famous monomer fraction data. While this could set the theoretical basis of these theories in doubt, we also show in this work that the findings with these association models are in agreement with a recently presented theory which links monomer fraction to dielectric constants. This new theory, like the three thermodynamic models, predicts more hydrogen bonding in water than Luck’s data (Angew. Chem. Int. Ed. Engl. 1980, vol. 19, pp. 28). Moreover, it appears that both the new theory and the three models provide evidence for the four-site association scheme for water and thus support that the tetrahedral structure of the water molecule is correct or at least that the tetrahedral structure is in agreement with several pure water physical properties, monomer fraction information and phase equilibria data in mixtures with alkanes.

An electrolyte CPA equation of state for mixed solvent electrolytes

Despite great efforts over the past decades, thermodynamic modeling of electrolytes in mixed solvents is still a challenge today. The existing modeling frameworks based on activity coefficient models are data-driven and require expert knowledge to be parameterized. It has been suggested that the predictive capabilities could be improved through the
development of an electrolyte equation of state. In this work, the Cubic Plus Association (CPA) Equation of State is extended to handle mixtures containing electrolytes by including the electrostatic contributions from the Debye-Hückel and Born terms using a self-consistent model for the static permittivity. A simple scheme for parameterization of salts with a limited number of parameters is proposed and model parameters for a range of salts are determined from experimental data of activity and osmotic coefficients as well as freezing point depression. Finally, the model is applied to predict VLE, LLE, and SLE in aqueous salt mixtures as well as in mixed solvents.

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**Development of an Electrolyte CPA Equation of state for Applications in the Petroleum and Chemical Industries**

This thesis extends the Cubic Plus Association (CPA) equation of state (EoS) to handle mixtures containing ions from fully dissociated salts. The CPA EoS has during the past 18 years 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 reduces 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 reusing 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
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.

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Process Design of Industrial Triethylene Glycol Processes Using the Cubic-Plus-Association (CPA) Equation of State
The Cubic-Plus-Association (CPA) equation of state (EoS) has already been proven to be a successful model for phase
equilibrium calculations for systems containing glycols. In the present work, we interface a thermodynamic property
package (Thermo System), based on CPA, with Aspen HYSYS through the CAPE-OPEN standards. We, then, simulate
certain binary and multicomponent systems where experimental data are available in the literature and which are critical
for process design of natural gas dehydration units by triethylene glycol (TEG). We also demonstrate the potential of CPA
for the process design of liquid-liquid extraction of aromatic hydrocarbons by TEG. Comparisons between simulation and
experimental results are presented in order to illustrate the reliability of Thermo System while it is used in a process
simulator for industrial applications. Detailed analysis on selecting TEG pure compound parameters and on calculating
TEG-water binary parameters is shown. Missing binary interaction parameters are regressed and presented for various
binary systems, and a relationship between the interaction parameters and alkane molecular weight is obtained for TEG-
alkane binary systems. A simulation case study of a typical natural gas dehydration process is also presented.

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Modeling of Dielectric Properties of Aqueous Salt Solutions with an Equation of State

The static permittivity is the most important physical property for thermodynamic models that account for the electrostatic interactions between ions. The measured static permittivity in mixtures containing electrolytes is reduced due to kinetic depolarization and reorientation of the dipoles in the electrical field surrounding ions. Kinetic depolarization may explain 25–75% of the observed decrease in the permittivity of solutions containing salts, but since this is a dynamic property, this effect should not be included in the thermodynamic modeling of electrolytes. Kinetic depolarization has, however, been ignored in relation to thermodynamic modeling, and authors have either neglected the effect of salts on permittivity or used empirical correlations fitted to the measured static permittivity, leading to an overestimation of the reduction in the thermodynamic static permittivity. We present a new methodology for obtaining the static permittivity over wide ranges of temperatures, pressures, and compositions for use within an equation of state for mixed solvents containing salts. The static permittivity is calculated from a new extension of the framework developed by Onsager, Kirkwood, and Fröhlich to associating mixtures. Wertheim’s association model as formulated in the statistical associating fluid theory is used to account for hydrogen-bonding molecules and ion–solvent association. Finally, we compare the Debye–Hückel Helmholtz energy obtained using an empirical model with the new physical model and show that the empirical models may introduce unphysical behavior in the equation of state.

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Modeling of dielectric properties of complex fluids with an equation of state

The static permittivity is a key property for describing solutions containing polar and hydrogen bonding compounds. However, the precise relationship between the molecular and dielectric properties is not well-established. Here we show that the relative permittivity at zero frequency (static permittivity) can be modeled simultaneously with thermodynamic properties. The static permittivity is calculated from an extension of the framework developed by Onsager, Kirkwood, and Fröhlich to associating mixtures. The thermodynamic properties are calculated from the cubic-plus-association (CPA) equation of state that includes the Wertheim association model as formulated in the statistical associating fluid theory (SAFT) to account for hydrogen bonding molecules. We show that, by using a simple description of the geometry of the association, we may calculate the Kirkwood g-factor as a function of the probability of hydrogen bond formation. The results show that it is possible to predict the static permittivity of complex mixtures over wide temperature and pressure ranges from simple extensions of well-established theories simultaneously with the calculation of thermodynamic properties. © 2013 American Chemical Society.

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Approach to Improve Speed of Sound Calculation within PC-SAFT Framework

An extensive comparison of SRK, CPA and PC-SAFT for speed of sound in normal alkanes has been performed. The results reveal that PC-SAFT captures the curvature of speed of sound better than cubic EoS but the accuracy is not satisfactory. Two approaches have been proposed to improve PC-SAFT’s accuracy for speed of sound: (i) putting speed of sound data into parameter estimation; (ii) putting speed of sound data into both universal constants regression and parameter estimation. The results have shown that the second approach can significantly improve the speed of sound (3.2%) prediction while keeping acceptable accuracy for the primary properties, i.e. vapor pressure (2.1%) and liquid density (1.5%). The two approaches have also been applied to methanol, and both give very good results.
Comparison of the Debye–Hückel and the Mean Spherical Approximation Theories for Electrolyte Solutions

The thermodynamics of electrolyte solutions has been investigated by many scientists throughout the last century. While several theories have been presented, the most popular models for the electrostatic interactions are based on the Debye–Hückel and mean spherical approximation (MSA) theories. In this paper we investigate the differences between the Debye–Hückel and the MSA theories, and comparisons of the numerical results for the Helmholtz energy and its derivatives with respect to temperature, volume and composition are presented. The investigation shows that the nonrestricted primitive MSA theory performs similarly to Debye–Hückel, despite the differences in the derivation. We furthermore show that the static permittivity is a key parameter for both models and that in many cases it completely dominates the results obtained from the two models. Consequently, we conclude that the simpler Debye–Hückel theory may be used in connection with electrolyte equations of state without loss of accuracy.

Process simulation of CO₂ capture with aqueous ammonia using the Extended UNIQUAC model

The use of aqueous ammonia is a promising option to capture carbon dioxide from power plants thanks to the potential low heat requirement during the carbon dioxide desorption compared to monoethanolamine (MEA) based process. The patented Chilled Ammonia Process developed by Alstom absorbs carbon dioxide at low temperature (2–10°C). The low temperature limits the vaporization of ammonia in the absorber and entails precipitation of ammonium carbonate compounds, thereby allowing high loadings of CO₂. The process has thereby good perspectives. However, a scientific understanding and evaluation of the process is necessary. In this work, the performance of the carbon dioxide capture process using aqueous ammonia has been analyzed by process simulation. The Extended UNIQUAC thermodynamic model available for the CO₂–NH₃–H₂O system has been implemented in the commercial simulator Aspen Plus® by using a newly developed user model interface (Maribo-Mogensen et al., submitted for publication). It allows for making equilibrium calculations using the advanced thermodynamic model together with the features of the commercial simulator. The present work deals with the results from the process simulation study. Two process configurations have been tested and a thorough sensitivity analysis of the main process parameters has been performed in order to analyze their effects on the heat and electricity requirement. This work confirms the high potential of the process. The heat requirement is found to be in the same range as the values reported recently for advanced amine processes. Assuming that cold cooling water is available, the electricity consumption remains limited. Hence the Chilled Ammonia Process is a promising option for post
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**Solids Modelling and Capture Simulation of Piperazine in Potassium Solvents**
Piperazine is an amine which is used both as an activator or promoter, but also as active component in CO2 capture solvents. High concentrations are being formulated to draw benefit of the PZ properties. This results in a risk of precipitation of PZ and other solid phases during capture. It could be a benefit to the capture process, but it could also result in unforeseen situations of potential hazardous operation, clogging, equipment failure etc. Security of the PZ process needs to be in focus. Flow assurance requires additional attention, especially due to the precipitation phenomenon. This entails all parts of the streams, but also during formulation and transport of the solvent. In this work the extended UNIQUAC thermodynamic model is presented with the addition of piperazine (PZ or PIPH2) in combination with the potassium ion of mixtures with CO2 in equilibration with KOH-KHCO3-K2CO3. Phase boundaries are laid out which shows the concentration regions of solid formation. A special focus will be given to the boundary where precipitations occur. The model is a generic. It builds on consistent parameters of the extended UNIQUAC model previously published. It allows for accurate vapor liquid equilibrium (VLE) calculation, heat capacity determination, and similar thermodynamic properties. It especially allows for determination of solid liquid equilibria (SLE) and heat of absorption/heat of desorption which are core variables in the determination of energy requirements for CO2 capture. In this work the typical phase behavior will be shown for the PZ solvent with potassium (K2CO3/KHCO3) for CO2 capture. Conclusions are given on a solvent compositions resulting in low heat requirements using the predictive nature of the extended UNIQUAC model. Concentration of a PZ/K2CO3 solvent is suggested with a heat of absorption/desorption of 40kJ/mol.

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