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Application of GC-PPC-SAFT EoS to amine mixtures with a predictive approach

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ABSTRACT

The GC-PPC-SAFT equation of state (EoS) is a combination of a group contribution method [S. Tamouza et al., Fluid Phase Equilib. 222–223 (2004) 67–76; S. Tamouza et al., Fluid Phase Equilib. 228–229 (2005) 409–419] and the PC-SAFT EoS [J. Gross, G. Sadowski, Ind. Eng. Chem. Res. 40 (2001) 1244–1260] which was adapted to the polar molecules [D. Nguyen-Huynh et al., Fluid Phase Equilib. 264 (2008) 62–75]. It is here applied to the vapour pressure and liquid molar volume of primary, secondary and tertiary amines and their mixtures with n-alkanes, primary and secondary alcohols, using previously published group parameters. The mixing enthalpy is also evaluated for the binary systems. Binary interaction parameters k_{ij} are computed using a group-contribution pseudo-ionization energy, as proposed by Nguyen-Huynh [D. Nguyen-Huynh et al., Ind. Eng. Chem. Res. 47 (2008) 8847–8858]. A unique corrective parameter for the cross-association energy between amines and alcohols is used.

The agreement with experimental data in correlation and prediction were found rather encouraging. The mean absolute average deviation (AAD) on bubble pressure is about 3.5% for pure amines. The mean AAD on the vapour–liquid equilibria (VLE) are respectively 2.2% and 5.5% for the amine mixtures with n-alkanes and alcohols. The AADs on saturated liquid volume are about 0.7% for the pure compounds and 0.9% for the mixtures. Prediction results are qualitatively and quantitatively accurate and they are comparable to those obtained with GC-PPC-SAFT on previously investigated systems.

1. Introduction

Amine aqueous solutions are very often used in the chemical absorption of CO_2 from postcombustion flue gases. This technology is of major importance but solvent regeneration is generally very energy intensive. Many research works are therefore conducted in order to find new solvents characterized by a high absorption capacity and a low heat of regeneration [1]. In this context, our objective is to develop a predictive thermodynamic model that will be able to screen a large amount of amines and alkanolamines aqueous solutions to find the required thermodynamic properties in the presence of CO_2. Phase equilibrium as well as enthalpic behaviour must therefore be investigated. In this work, only vapour–liquid equilibrium (VLE) and excess enthalpy (H^E) of amines and their mixtures with n-alkanes and alcohols are discussed, as a first step.

Aliphatic amines are the organic derivatives of ammonia, where one or more hydrogen atoms are substituted by an alkyl group. Primary (RNH_2), secondary (R_2NH) or tertiary (R_3N) amines can be found. They are polar and primary and secondary amines are self-associative, which results in numerous nonidealities in their solutions with other molecules, in particular with alcohols and water.

Possible models for these polar and hydrogen-bonding mixtures are numerous. Among the first developments that discuss this kind of systems, we can mention the quasi-chemical theory of Guggenheim [2], the Non Random Two-Liquid Theory (NRTL) of Renon and Prausnitz [3] or another local composition based UNIQUAC model of Abrams and Prausnitz [4]. The Associated Perturbed-Anisotropic-Chain Theory (APACT) [5] which, for the associative molecules, introduces the enthalpy and entropy of association can also be used. In the early nineties, the SAFT model (Statistical Associating Fluid Theory), initially developed by Chapman et al. [6–8] has made available an explicit treatment of association within an equation of state framework. Among the most extensively used versions of SAFT we can mention the original CK-SAFT [9], PC-SAFT [10] and SAFT-VR [11]. The cubic-plus-association (CPA) equation of state (EoS) [12,13] uses the same theory, coupled with a cubic equation of state.

The SAFT family of equations of state has been improved by considering the effect of polarity, as an additional correction on the reference term. Without being exhaustive, we can mention the so-called 'molecule' approaches, with the breakthrough paper

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of Kraska and Gubbins [14] for dipole–dipole interactions, and the 'segment' approach, initiated by the group of Chapman who introduces the molecular chain concept [15]. Using the PC-SAFT EoS, Gross and co-workers [16,17] have developed an alternative approach for dipolar and quadrupolar molecules based on two centered Lennard-Jones molecular simulation data. Their equation is now called PCP-SAFT. Karakatsani and Economou [18] assume that the polar contribution is spread over the entire chain rather than located on a single segment. They use both PC-SAFT and a truncated version, used to simplify the equation. The proposal of Nguyen-Huynh et al. [19], who use the approach proposed by Jog and Chapman [15] with the PC-SAFT EoS, thus using the PPC-SAFT terminology, is chosen in this work. Regarding SAFT-VR, a similar extension was proposed by Zhao and McCabe [20].

An important improvement to the available models is the group contribution method which renders them more predictive and allows investigating systems for which experimental data are not available. The group contribution (GC) methods are widely applied to predict almost all thermodynamic properties. The most basic methods allow predicting more or less accurately the pure component properties, such as normal melting and boiling points, critical properties, acentric factor or different enthalpies. In these methods, required pure compound properties are calculated summing the contribution of each functional group occurring in the molecule. Among the numerous available approaches we can mention the ones proposed by Joback and Reid [21], Ambrose [22], Lydersen [23] or Constantinou and Gani [24].

This kind of methods was an inspiration for more complex models which, using GC approaches, are able to calculate not only the pure component physical properties (e.g. vapour pressure or liquid density) but also the mixture characteristics (such as VLE and LLE, infinite dilution activity coefficient, excess enthalpy, Henry's law constant and partition coefficient). As a well-known example of GC methods, UNIFAC (UNIversal quasi-chemical Functional group Activity Coefficient) [25,26] must be mentioned, which is an activity coefficient model based on UNIQUAC [4]. This very fast and simple method has been applied to numerous systems, and modified in order to extend its scope [27,28]. It can be used when experimental data are not available. However, as all activity coefficient models, it is limited to low pressures and is difficult to apply for very asymmetric systems containing both gases and liquids.

An equation of state is needed for high pressure, asymmetric systems. This is why UNIFAC has been implemented, using Gibbs Excess (G^E) mixing rules, into cubic equations of state, thus giving rise to PSRK (predictive Soave–Redlich–Kwong) [29], or more recently VTPR (Volume Translated Peng–Robinson) [30]. The PPR78 equations are also based on the group contribution concept [31]. The predictive power of this type of equations reaches its limit when the molecules are very polar or solvating. This is why the group contribution concept has been extended to the SAFT theory.

Among the first approaches to combine Wertheim's association theory with a group contribution concept, one should mention the Group Contribution Association EoS (GCA) [32–34]. With regard to the SAFT family, the first authors who propose to apply the GC concept are Vijande et al. [35], using PC-SAFT on hydrofluoroethers. Soon after, Tamouza et al. used this concept for hydrocarbons [36] and their mixtures [37], using the original SAFT and SAFT-VR. Later, this same group also included PC-SAFT using the same GC concept [38,39]. Tihic et al. extended the group contribution concept with a simplified version of PC-SAFT, to a large number of groups, and included second order groups for improving the predictions, and distinguishing among isomers [40,41]. A new concept was proposed with the SAFT-γ theory, that is based on SAFT-VR but regards the molecule as fused heteronuclear united-atoms groups [42,43]. In SAFT-γ the binary interaction parameters can be obtained directly from the pure compounds properties. The GC-SAFT-VR model proposed by Peng et al. [44] uses a similar approach, but does not consider the fact that the segments are fused, thus reducing the number of parameters. In addition, it allows taking into account the connectivity between segments. A final application of GC in both the original SAFT and PC-SAFT but also to EDS EoS (Elliott–Suresh–Donohue) [45] was proposed by Emami et al. [46]. They propose to fix all parameters that can be considered transferable (in particular association parameters) and to correlate the remaining EoS parameters to a number of physical quantities (compressibility factor, solubility parameter, and boiling temperature) which themselves can be obtained from GC methods.

Regarding amine containing mixtures, a number of papers use SAFT models for describing the vapour–liquid equilibrium behaviour of water + acid gas + amines [47–49]. The CPA model has also been used to investigate these systems [50]. These papers all focus on small size molecules (monoethanolamine or diethanolamine), and show that the association models used are adequate to describe these systems. However, each binary system must be treated separately and experimental data are needed for this purpose. They can therefore not be considered as predictive. Sanchez et al. [34], on the opposite, use a group contribution EoS (GCA [51]) which appears to be very accurate on the investigated systems, however it require a large number of transferable interaction parameters.

Previous investigations by Nguyen-Huynh et al. [19] on other polar systems make us believe that the group contribution version of the polar PC-SAFT EoS (GC-PPC-SAFT) is promising for describing both polar and associating systems. The GC-PPC-SAFT model has been successfully applied to numerous systems containing n-alkanes [36], alcohols [19,52] and esters [53].

In this work, the GC-PPC SAFT equation of state is applied to pure amines and mixtures with alkanes and alcohols, both from a correlation as from a predictive point of view. In later works, the description of the multifunctional alkanolamine molecules will be investigated as well as amines and alkanolamines mixtures with water. This requires additional examination in order to take into account the multifunctional character of alkanolamines and in view of the possible presence of liquid–liquid demixtion in the case of amine + water systems.

In the next section we present the theoretical introduction to the GC-PPC-SAFT structure and parameterisation. The mixing and combining rules are provided. Then, determination of the parameters and the correlation results are discussed in Section 3. Subsequently the predictive capacities of the model followed by a discussion of the results are presented in Sections 4 and 5.

2. The GC-PPC-SAFT model

2.1. PPC-SAFT

Numerous versions of the SAFT (Statistical Associating Fluid Theory) model have been presented in the last few years [6,11,54–57]. The equation used in this work is based on the group contribution method proposed by Tamouza [36,37,52] coupled with the PC-SAFT proposed by Gross and Sadowski [10]. It is next extended to polar molecules by Nguyen-Huynh [19] using the theory of Gubbins and Twu [58] for spherical molecules and the segment approach of Jog and Chapman [15] for chain molecules. Hence PPC-SAFT stands for Polar Perturbed Chain Statistical Associating Fluid Theory. The equation of state is generally written based on the residual Helmholtz free energy A^{res} which is a sum of a reference term (here the hard chain) and different perturbation contributions:

$$A^{res} = A^{hc} + A^{disp} + A^{chain} + A^{assoc} + A^{multi\text{-}polar} \quad (1)$$