

## Long chain multifunctional molecules with GC-PPC-SAFT: Limits of data and model

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### ABSTRACT

The Group Contribution Polar Perturbed Chain Statistical Associating Fluid Theory (GC-PPC-SAFT) equation of state is here extended to the long chain multifunctional molecules as alkanolamines and alkanediols. The limits of data and model are discussed. For this, plots presenting the vapourization enthalpy ( $\Delta h_{T_b}^v$ ) as a function of normal boiling temperature ( $T_b$ ) are used. The trend of the published data for alkanediols is found difficult to interpret using the theory. Supplementary data are generated from molecular simulations in order to further analyse the behaviour of this family, but the conclusion is that additional measurements are needed.

The monofunctional (n-alkanes, primary alcohols and primary amines) and long chain multifunctional (diamines, alkanolamines and alkanediols) molecules are compared in the homologous series. The trends have led to modify the model parameters using the vapour pressure and the saturated liquid phase volume data. Two additional alcohol group (OH) parameters than these proposed by Nguyen-Huynh [D. Nguyen-Huynh et al., Fluid Phase Equilib. 264 (2008) 62–75] have been introduced. They are needed when the molecule has more than one associating group in its chain.

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### 1. Introduction

Multifunctional molecules are of widespread interest in many industrial fields. Due to their associating properties, among others, they are commonly used as solvents or co-solvents. Alkanolamines find their application mainly in the processes of acid gases removal, especially natural gas treatment and CO<sub>2</sub> capture. The polyalcohols are widely used in oil industry for gas dehydration (monoethylene glycol called also 1,2-ethanediol (MEG) and its oligomers such as diethylene glycol (DEG) or triethylene glycol (TEG)) or in the synthesis of polyesters as anti-freeze agents ( $\alpha,\beta$ -alkanediols). The correct description of the thermophysical properties of these molecules is thus crucial in the design and optimization of a large number of industrial processes.

The ultimate goal of this research is to develop a predictive thermodynamic model that will be able to describe the phase equilibria of amine–water systems in the presence of CO<sub>2</sub>. This kind of model can be useful to screen the absorption capacities of numerous amines and alkanolamines, making it possible to find the best solvent featuring a high absorption capacity and a low heat of regeneration. The first step of this work was a description of the physical equilibria of monofunctional molecules and their mixtures

with hydrocarbons and alcohols. A recent publication extends the GC-PPC-SAFT model to amines and some simple mixtures [1]. Yet, most industrial solvents work with multifunctional molecules (in particular alkanolamines). Hence, this work focuses on the extension of the model to this kind of molecules.

Up to now relatively few papers concerning multifunctional molecules exist, which is probably due to the limited data available and difficulties related to the description of these kinds of systems. Surprisingly, in available publications, authors usually focus very briefly on pure compounds (typically such as monoethanolamine (MEA), diethanolamine (DEA) or 1,2-ethylenediol (MEG)) and describe in many details the mixtures of these multifunctional species with water, hydrocarbons, alcohols and acid gases (CO<sub>2</sub> or H<sub>2</sub>S). In this paper we propose to investigate the pure components behaviour. The proposed analysis leads to the improvement of the predictive capacities of the model.

Among the different models to evaluate the alkanolamines and their mixtures, we can mention the one proposed by Sanchez et al. [2] which, using the GCA equation of state (EoS), predict the phase behaviour of MEA, DEA and methyl diethanolamine (MDEA)+water mixtures as well as the hydrocarbons solubility in aqueous alkanolamine solutions. Austgen et al. [3] as well as Barreau et al. [4] have used the e-NRTL model to describe the CO<sub>2</sub>/H<sub>2</sub>S–water–alkanolamine mixtures. The refined e-NRTL model has been applied by Hessen et al. [5] to CO<sub>2</sub>–water–alkanolamine systems. Avlund et al. [6,7] have applied CPA and sPC-SAFT

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**Table 1**

Group contribution parameters for amine, n-alkane and alcohol series with GC-PPC-SAFT. Bold parameters have been determined in this work.

Group	Reference and chain terms			Association					Polarity		Ref.	
	$(\varepsilon/k)/K$	$\sigma/\text{\AA}$	$R_1$	$R_2$	$R_3$	Type	$(\varepsilon^{AB}/k)/K$	$\kappa_0^{AB}$	$\kappa_1^{AB}$	$\mu/D$		$x_p m$
CH <sub>3</sub>	189.9628	3.4873	0.7866									[36,37]
CH <sub>2</sub>	261.0866	3.9308	0.3821									
CH	402.0232	4.9252	0.2000									[36]
OH <sup>a</sup>	307.5094	2.8138	0.8318	<b>0.7432<sup>b</sup></b>		3B	2143.3	0.00885	<b>0.006374</b>	1.7	0.50	[22], this work
NH <sub>2</sub>	341.8956	2.8347	0.8242			2B	950.0	0.01733		1.5	0.40	[1]
NH	334.3947	3.6655	0.4723 <sup>c</sup>	0.1878	0.3328	2B	500.0	0.09248		1.0	0.55	
NCH <sub>3</sub>	342.6160	4.1494	0.5419							1.0	0.55	

<sup>a</sup> Primary alcohol group.<sup>b</sup> New chain contribution parameter for alkanediols only.<sup>c</sup> Value of  $R$  of the secondary amine group is calculated as  $R(p) = R_2 + R_3/p$  where  $p$  is the position of the NH group within the chain (i.e. the smallest integer number of carbons from the chain end). This equation is applied when  $p \geq 2$ . In the case when  $p = 1$  the parameter  $R$  should be used directly.

to mixtures of MEA, DEA and MDEA with hydrocarbons, water and alcohols. Among other applications of SAFT models to alkanolamines we can mention: Button and Gubbins [8] which have applied CK-SAFT to MEA/DEA–water–CO<sub>2</sub> systems, Nasrifar and Tafazzol [9] which have described CO<sub>2</sub>/H<sub>2</sub>S–water–alkanolamine systems with PC-SAFT and Mac Dowell et al. [10] which have used SAFT-VR to model CO<sub>2</sub>–MEA–water system.

Regarding polyalcohols most publications concern ethylene glycol and its oligomers (DEG, TEG, ...). Most of the time, vapour pressures and liquid densities are first evaluated. The behaviour of their mixtures typically with alkanes, other alcohols, water and/or CO<sub>2</sub> are then correlated or predicted. Models such as CPA [11–14], NRHB [14], ESD [15], and SAFT [16–19] have been used for this purpose.

In contrast, our aim is to understand the evolution of  $\alpha, \beta$ -alkanediols in their homologues series and not the oligomers. On this topic, beyond 1,2-ethanediol (MEG) and its mixtures, which are included in almost all papers discussed above, we found only one paper by Li and Englezos [18] which additionally describe 1,2-propanediol, 1,3-propanediol and their mixtures using the SAFT EoS.

The majority of the above models are not predictive, which considerably limits their extension to other multifunctional molecules for which no experimental data is available. Some models can be considered as only partially predictive: they are not predictive for pure compounds (molecule specific parameters are required) but they are predictive for some mixtures: if there is no binary interaction parameter or if the ternary mixtures are described using previously regressed binary interaction parameters. A predictive model for pure components is one whose parameters can be determined without experimental data. Such are, for example, the equations that use a group contribution method such as GCA EoS [2].

In this work we chose to use the Group Contribution Polar Perturbed Chain Statistical Associating Fluid Theory (GC-PPC-SAFT) equation of state, which is a combination of a group contribution method proposed by Tamouza et al. [20] and the PC-SAFT EoS proposed by Gross and Sadowski [21], next extended to polar molecules by Nguyen-Huynh et al. [22]. More details on GC-PPC-SAFT can be found in previous works [20,22,23].

When attempting to evaluate the quality of the model on multifunctional molecules, we first came up with the problem of data consistency. The data analysis is therefore the first part of this work. As a second step, we have examined the predictive capacity of GC-PPC-SAFT for the alkanolamine and alkanediol molecules and propose some improvement.

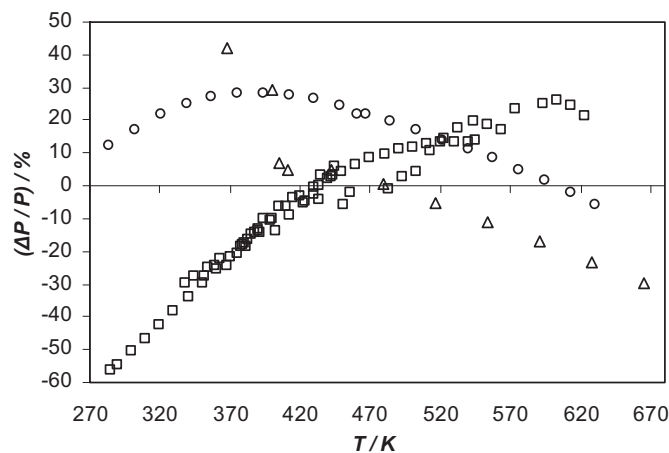
## 2. Problem statement

In the GC-PPC-SAFT model, the molecules are presented as a sum of spherical interconnected segments. Each molecule is characterized by its parameters which are calculated using the

group contribution method that was already presented in our recent paper [1]. In this latter work, four new functional groups (NH<sub>2</sub>), (NH), (NCH<sub>3</sub>) and (N(CH<sub>3</sub>)<sub>2</sub>) have been defined and successfully tested with mixtures of alkylamines and n-alkanes or alcohols molecules. More details regarding the model and its parameterization are given in Appendix A. All group parameters used in this work and their origin are listed in Table 1.

It is expected that the application of the group contribution approach will make it possible to calculate the properties of complex multifunctional molecules, as alkanolamines in a predictive manner. This was attempted using the DIPPR experimental vapour pressure data [24] of three compounds, as shown in Fig. 1. It appears that the deviations are larger than expected. For all three molecules the AADs are around 17% which is 3–4 times bigger than those previously obtained in prediction for monofunctional molecules using the same model (around 4.5 and 7% in prediction respectively for pure amines [1] and alcohols [22]). The estimated uncertainties of the data according to the DIPPR source are 10% for monoethanolamine, 5% for 3-amine-1-propanol and 10% for 6-amino-1-hexanol (especially at low temperature). Moreover no real trend is observed: for 6-amino-1-hexanol, the deviation is positive for the lower temperatures and negative for the elevated ones; for monoethanolamine the trend is inverted, while for 3-amino-1-propanol, shows accurate results for the lowest and highest temperatures, and a large positive deviation in the middle of the temperature range.

When a model is not able to correctly fit the data, either the model is wrong or the data are bad. In order to verify the quality of either, a thermodynamic consistency check should be performed,



**Fig. 1.** Deviations of the GC-PPC-SAFT model to the vapour pressure experimental data [24] for (□) monoethanolamine, (○) 3-amino-1-propanol and (Δ) 6-amino-1-hexanol.

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