Chemical Engineering Thermodynamics

Computational Chemistry for the Parameterization of Equations of State and Other Models

In a recently-started research topic, computational chemistry (Density Functional Theory, DFT) was used to determine non-randomness factors (and lattice coordination numbers) for 50 chemical species at 298.15 K and 0.1 MPa, providing an enhanced physical meaning to these parameters. Then, the obtained non-randomness factors were used to correlate ternary liquid-liquid equilibria (LLE) data using different excess Gibbs free energy models. On the other hand, the parameterisation of the Cubic Plus Association (CPA) equation of state was successfully achieved by finding correlations between parameters (*e.g.*, co-volume) and properties (*e.g.*, critical temperature and pressure) or only between parameters. This way, pure component parameters were predicted without having to fit the model to liquid density and vapour pressure data.

Objectives

The non-randomness factor (α) is related to the polarity (and consequent randomness of spatial orientation) of the molecules and is generally fixed between 0.20 and 0.47. Theoretically, this parameter goes from 0 (completely random spatial orientation) to 1 (completely defined spatial orientation), with the former state being associated to zero polarity while the latter corresponds to an extremely high polar asymmetry, but no technique has been developed so far for its accurate estimation. In fact, the consideration of a constant non-randomness factor for mixtures is known to harden azeotrope description and to cause convergence issues in both the Non-Random Two-Liquid (NRTL) and UNIversal QUAsi Chemical (UNIQUAC) models, which are the most applied excess Gibbs free energy models in the correlation of liquid-liquid equilibria (LLE) data. Hence, novel methodologies are needed for the parameterisation of the non-randomness factors to improve the modelling of phase equilibria.

Density Functional Theory (DFT) is an *ab initio* computational quantum mechanical modelling methodology used in various fields of physics and chemistry, and its primary application is to investigate the electronic (or nuclear) structure of many-body systems, such as atoms and molecules. DFT derives from the methods of Thomas−Fermi and Hartree−Fock−Slater and can predict material properties for new systems without any experimental input, so it could become the basis of the parameterisation of excess Gibbs free energy models, such as NRTL and UNIQUAC.

On the other hand, the Cubic Plus Association (CPA) equation of state (EoS) combines the Soave-Redlich-Kwong (SRK) EoS with the association term of the Wertheim theory and is widely used in the petroleum industry given its high accuracy and small computing time. This EoS requires from 3 to 5 parameters to correctly describe a chemical species: three parameters (co-volume, b, and the energy parameters a_0 and c_1) for non-associating compounds, *i.e.,* which are unable of establishing hydrogen bounds, and two extra (association energy, ϵ, and the volume of association, β) for associating compounds. However, a high number of parameters is still to determine, especially for electrolytes, ionic liquids, pharmaceuticals, polymers and other heavy compounds, so there is a significant need of finding ways of predicting them.

Current Development

The non-randomness factors (and lattice coordination numbers) of 50 chemical species (including, for example, alcohols and alkanes) were estimated at 298.15 K, 0.1 MPa and liquid state using computational chemistry. The calculations were carried out at Density Functional Theory (DFT) level using the GAUSSIAN G09 programme. To do so, a combination of the DFT hybrid functional B3LYP with the basis set 6-311++G was used, and the molecules were optimized simulating a cavity within a liquid solvent (composed of molecules of their own) using the Polarizable Continuum Model (PCM).

In these studies, as Fig. 1 shows, it was found that larger dielectric constants favoured larger non-randomness factors (more defined spatial orientations of the molecules). For example, a value of 0.3333 was obtained for water, which is in surprising agreement with the common application of $\alpha = 0.3$ for aqueous mixtures. Moreover, benzene did not attain the lowest value amongst the aromatics despite its well-known equal charge distribution amid the carbon atoms. Substituting aromatic hydrogens by alkyl groups allowed for a larger area for the electronic cloud, probably decreasing the existent dipole moments. This behaviour was also found for linear alcohols, in which longer alkyl chains implied lower non-randomness factors in chemical species with odd (methanol (0.3242) > propan-1-ol (0.1970) > pentan-1-ol (0.1631) > heptan-1-ol (0.1482) > nonan-1-ol (0.1411) > undecane-1-ol (0.1362)) and even (ethanol (0.2345) > butan-1-ol (0.1874) > hexan-1-ol (0.1663) > octan-1-ol (0.1544) > decan-1-ol (0.0620) > dodecan-1-ol (0.0585)) number of carbons.

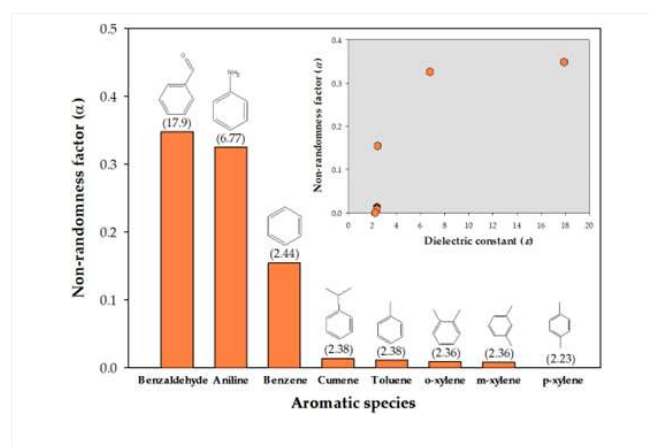Then, the validity of the determined parameters was tested

Fig 1. Determined non-randomness factors (α) at 298.15 K and 0.1 MPa for some similar aromatic species, with respective chemical structures and dielectric constants at 298.15 K (in parenthesis).

by correlating liquid-liquid equilibria (LLE) of 15 ternary systems (*e.g.*, {glycerol (1) + benzene (2) + methanol (3)} at 298.15 K and 0.1 MPa) using the Non-Random Two-Liquid (NRTL) and UNIversal QUAsi Chemical (UNIQUAC) models.

Even though no drastic difference was found in the description of systems, it was concluded that the proposed methodology would provide more specific non-randomness factors, which are expected to ease the interpretation of phase equilibria by better describing azeotropes, hinting non-ideality and allowing to infer solubility.

Collaboration with the Technical University of Denmark

In collaboration with the Technical University of Denmark (Denmark), a MSc student developed the master dissertation abroad under the Erasmus+ programme. This exchange was focused on compiling a database of properties (*e.g.*, critical temperatures (T_c), van der Waals parameters and molecular masses) for 197 chemical species, including, for example, alkanes, alcohols, ketones and fluorocarbons. This database also comprised the parameters of the Cubic Plus Association (CPA) equation of state (EoS) available in literature for these chemical components, and the main goal was to find correlations between parameters to enhance the predictive ability of this EoS. As Fig. 2 shows, promising trends were found for most of the analysed chemical species, particularly to what pertains parameters such as the energy term parameter (a_0), the co-volume (b) and the ionisation potential (I) with the van der Waals volume (V_w).

constituting a relevant step towards a more predictive CPA EoS.

Future Perspectives

The estimated non-randomness factors using computational chemistry only comprised ternary systems of neutral molecules, for which this methodology remains untested for more non-ideal systems, such as the ones containing electrolytes and mixed-solvents. Moreover, the Density Functional Theory (DFT) calculations were only performed in liquid state, so this novel approach cannot be applied to, for example, vapour-liquid equilibria (VLE) data.

Regarding the parameterisation of the Cubic Plus Association (CPA) equation of state (EoS), no correlations were found for the parameters which account for hydrogen bonding (association energy, ϵ, and the volume of association, β), even though these are the hardest to fit to liquid density and vapour pressure. Therefore, further research is needed to find alternative procedures to parameterise this equation of state and help decrease the need for copious experimental data relative to associating components.

For that purpose, computational chemistry could be used to describe solvation and improve the establishment of
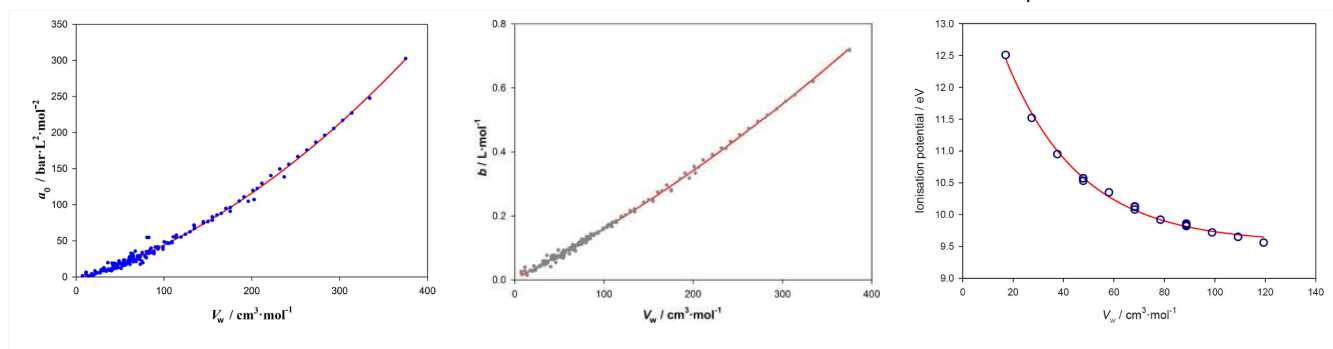

Fig 2. Some trends observed with the van der Waals volumes (V_w) for all species except fluorocarbons: *left* – energy term parameter (a_0); *centre* – co-volume (b); *right* – ionization potential (I).

After having found these correlations, they were used to predict the CPA parameters of other chemical species and applied in the estimation of vapour pressure and saturated liquid density. In this assessment, a temperature range of $(0.50 - 0.95) \cdot T_c$ with a step of 1 K was considered, and small deviations from the literature values (DIPPR) were obtained, as Fig. 3 shows. Furthermore, some other promising trends were noticed between the co-volume (b) parameter and the binary interaction parameters (k_{ij}), also
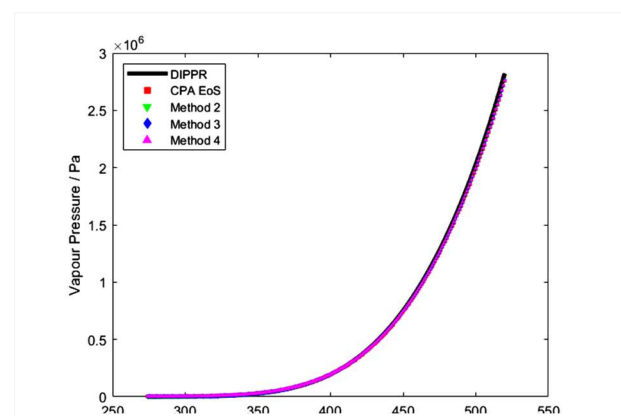
correlations between modelling parameters and physicochemical properties or just between parameters. Moreover, machine learning based on neural networks could also be applied to assist in the search for these patterns by greatly increasing the number of tested systems and make the process less time-consuming.

Finally, only the CPA EoS was delved into during this period, although the Perturbed Chain – Statistical Associating Fluid Theory (PC-SAFT) model also requires three parameters with a very specific physical meaning for pure and non-associating components (*e.g.*, length and diameter of segment). Hence, the same methodology could be extended to PC-SAFT to ease its application.

Related Sustainable Development Goals

Outputs

Master Dissertations

[1] P. Velho, Development of a more predictive Cubic Plus Association equation of state, MIEQ, DTU & FEUP, 2020.

Selected Publications

[1] P. Velho et al., Fluid Phase Equilib. 540, 113045 (2021)
[2] P. Velho et al., J. Chem. Eng. Data (2023)

Fig 3. Predicted vapour pressures for isobutanol using the CPA EoS with literature-based (□) and correlated (∇,◇,△)

Team

Eugénia A. Macedo, Professor & Group Leader; Elena Gómez, Researcher; **Pedro Velho**, PhD Student & MSc Student; **Leonor R. Barroca**, MSc Student.

Funding