Chemical Engineering Thermodynamics

Thermodynamic Modelling of Mixed-Solvent and Electrolyte-containing Systems

KEYWORDS: Mixed-solvents; Electrolytes; UNIQUAC; PDH+UNIQUAC; ePC-SAFT; Thermodynamic modelling.

Innovative approaches for the qualitative and quantitative evaluation of the degree of dissociation of ionic liquids were developed using the Pitzer-Debye-Hückel equation coupled with the UNIversal QUAsiChemical model (PDH+UNIQUAC). PDH+UNIQUAC was the preferred model for liquid-liquid equilibria (LLE) data correlation, while the extended Pitzer model of Archer was used for vapour-liquid equilibria (VLE). Moreover, the solubility of biomolecules (*e.g.*, amino acids) and their partition coefficients in Aqueous Two-Phase Systems (ATPS) were successfully predicted using a modified electrolyte Perturbed Chain-Statistical Associating Fluid Theory (ePC-SAFT) model.

Objectives

Ionic liquids, or molten salts, are salts which present a melting temperature below 373.15 K at 0.1 MPa. Therefore, they are frequently liquid at room temperature and pressure, which, together with their large solvent power, negligible vapour pressure and low toxicity, make them good alternatives for volatile organic compounds (VOCs). Additionally, they are considered very versatile solvents since it is possible to easily tune their physicochemical properties by changing the constituent salt cations and anions. For this reason, they are widely known as "designer solvents". Nevertheless, their high viscosity and surface tension, together with a scarce knowledge on their ability to dissociate in solution, have been delaying their application and hardening an accurate thermodynamic modelling.

Second, the presence of electrolytes (salts) in solution is known to decrease the vapour pressure of the solvents and to advocate nonideal behaviour, so the modelling of vapour pressure osmometry (VPO) data (*e.g.*, osmotic and activity coefficients) is essential to the parameterisation and improvement of equations of state and excess Gibbs free energy models. In addition to vapour-liquid equilibria (VLE) data, the correlation of liquid-liquid equilibria (LLE) is also particularly important for the development and optimization of chemical processes, but the absence of a specific physical meaning for most parameters undermines their interpretation.

Aqueous Two-Phase Systems (ATPS) are a promising liquid-liquid extraction technique constituted by aqueous mixtures of two highly water-soluble species, such as two polymers, a polymer + salt (*e.g.*, polyethylene glycol and tripotassium citrate), and an organic solvent + salt (*e.g.*, ethyl lactate + disodium tartrate). ATPS are commonly applied in the extraction of electrolytes with antioxidant activity (*e.g.*, ferulic acid and epicatechin), but the presence of the mentioned salts in the extractive media complicates an already intricate thermodynamic modelling. Therefore, it is vital to find novel predictive approaches for the partition of electrolytes in ATPS.

Current Development

A novel methodology of calculating the closest approach parameter of ionic liquids, which is related to the distance between salt ions, was developed supposing total, partial or no dissociation (as Fig. 1 shows). This approach allowed to qualitatively evaluate the degree of dissociation (or ionicity)

of 13 ionic liquids (*e.g.*, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) in aqueous binary mixtures.

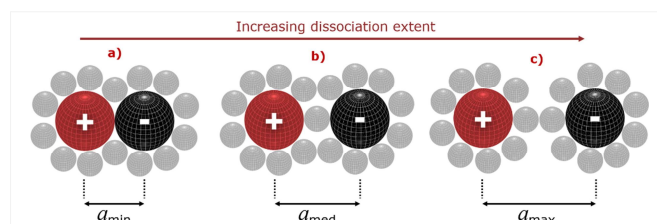For that purpose, the Pitzer-Debye-Hückel equation was coupled with the UNIversal QUAsiChemical model

Fig. 1 - Influence of solvation on the hard-core collision diameter, which is needed for the calculation of the closest approach parameter.

(PDH+UNIQUAC). Even though the developed methodology was corroborated by ionicity (or degree of dissociation or dissociation extent) data from experimental determinations, it failed to quantify dissociation.

Therefore, a refined approach was developed preserving the PDH+UNIQUAC model but based on solubility data from literature. Moreover, the description of the mixed-solvent properties (*e.g.*, dielectric constant and density) was enhanced and the closest approach parameter was calculated using the Pitzer-Simonson equation. This methodology allowed to quantify the dissociation extent of ionic liquids (*e.g.*, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) in the whole composition range for 31 different binary mixtures (*e.g.*, with water,
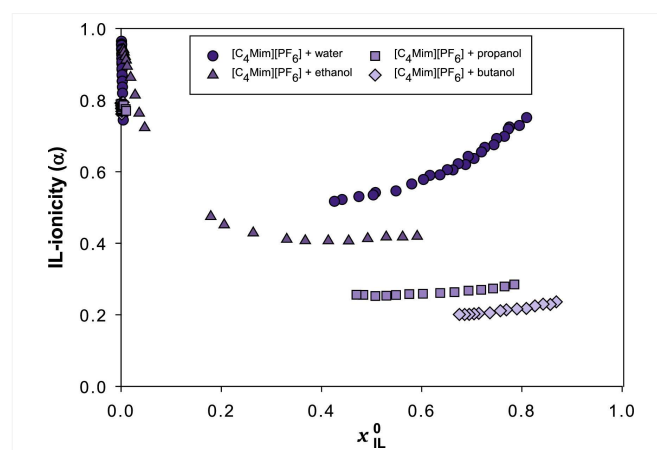

Fig. 2 - Predicted degree of dissociation (α) as a function of the mole fraction of ionic liquid, at atmospheric pressure, for 1-butyl-3-methylimidazolium hexafluorophosphate ([C4Mim][PF6]) with water, ethanol, 1-propanol or 1-butanol.

ethanol, propan-1-ol or butan-1-ol), as Fig. 2 shows. The validation of this technique was performed by comparing the obtained results with experimental determinations of ionicity from literature.

PDH+UNIQUAC was also applied in modelling liquid-liquid equilibria of newly-found Aqueous Two-Phase Systems (ATPS), such as {ethyl lactate (1) + potassium carbonate (2) + water (3)} at 298.15 K and 0.1 MPa, exhibiting a better

performance than classical UNIQUAC. Moreover, for ATPS based on ethyl lactate, the classical and electrolyte versions of the Non-Random Two-Liquid (NRTL) model were also applied, with the latter showing smaller deviations from experimental data due to the inclusion of an additional term for long-range interactions.

Concerning vapour pressure osmometry (VPO), the Modified Non-Random Two-Liquids (MNRTL) model was used to correlate the obtained osmotic and activity coefficients of aqueous solutions of organic salts (*e.g.*, sodium formate, disodium succinate, trisodium citrate) and polymers (*e.g.*, polyethylene glycol with 6000 g·mol^{-1}), and compared with the extended Pitzer model of Archer. While both models provided a reliable description of the studied systems, the extended Pitzer model of Archer generally achieved a more precise description of the experimental data.

Collaboration with the University of Vigo

A collaboration with the University of Vigo (Spain) was maintained for some months with the final goal of drafting a book chapter on the equilibrium description of electrolyte-containing systems. The final document was included as chapter 13 (Equilibrium in Electrolyte Systems) in the book "Thermodynamics of Phase Equilibria in Food Engineering", published in 2019 by Academic Press (Elsevier). The chapter comprised a thorough review of some thermodynamic models, such as the extended Pitzer model of Archer, and some notes on their application to vapour-liquid equilibria (VLE) and solid-liquid equilibria (SLE) in systems containing electrolytes and/or mixed solvents.

Collaboration with the Technical University of Dortmund

A collaboration with the Technical University of Dortmund (Germany) involved two research stays of PhD students. The performed research was based on the thermodynamic modelling of solubility and partition of biomolecules (*e.g.*, ascorbic acid, riboflavin, folic acid, and cyanocobalamin) in green Aqueous Two-Phase Systems (ATPS) using the classical and electrolyte versions of the Perturbed Chain-Statistical Associating Fluid Theory (PC-SAFT). This model, which was developed at the Technical University of Dortmund, was modified, yielding, for the first time, very satisfactory predictions of activity coefficients, partition coefficients and solubilities in this kind of systems. During investigation, it was noticed that the binary interaction parameters (BIPs) could be extrapolated from one system to another, increasing the predictiveness of the applied thermodynamic models in the description of polymer-based ATPS. Fig. 3 shows all the interactions considered by this model for the partition of vitamins in ATPS.
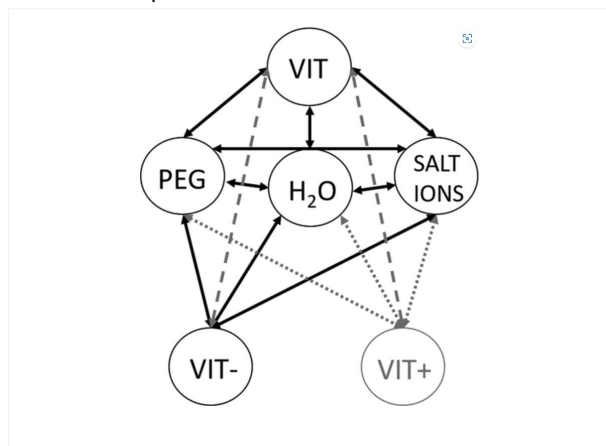

Fig. 3 – Considered interactions between the components present in biomolecule partitioning in Aqueous Two-Phase System (ATPS)

Future Perspectives

The developed methodologies for the estimation of the dissociation extent (or ionicity) of ionic liquids still cannot be applied to mixtures containing more than one ionic liquid, so further research is needed on this field. On the other hand, no thermodynamic models besides PDH+UNIQUAC were applied for this purpose even though they could be used following the same methodology. Moreover, the analysed chemical families of ionic liquids are still very narrow and the final application of these ionicity data (for example, in modelling the partition of biomolecules in ATPS based on ionic liquids) is still missing. Therefore, it is necessary to diversify the applied thermodynamic models and to include the obtained ionicity data in future modelling studies of the research group.

Although liquid density and vapour pressure data were obtained for different systems, these data were never used to parameterise equations of state nor excess Gibbs free energy models. This could be extremely useful to reduce the number of variables and to attribute a more concrete physical meaning to the adjustable parameters.

The application of the excess Gibbs free models to phase equilibria description still lacks any predictive character, for which they mostly correlate the obtained data. An increased predictiveness (for example, using machine learning) would help decrease lab work and ease the search for more favourable phase diagrams for extraction.

Related Sustainable Development Goals

Outputs

PhD Theses
[1] Kamila Wysoczanska, Solubility and partitioning of biomolecules. Experimental studies and modeling, PDEQB, FEUP, 2020.

Master Dissertations
[1] H. Marques, A New Approach on the Prediction of Dissociation of Ionic Liquids, MIEQ, FEUP, 2021.
[2] C. Lopes, Quantitative Prediction of the Dissociation Degree of Ionic Liquids in Binary Mixtures, MEQ, FEUP, 2022.

Book Chapters
[1] O. Rodríguez et al., Chapter 13: Equilibrium in Electrolyte Systems, pp. 529-562, Thermodynamics of Phase Equilibria in Food Engineering, Academic Press, 2019.

Selected Publications
[1] K. Wysoczanska et al., Ind. Eng. Chem. Res. 58, 7362-7369 (2019)
[2] K. Wysoczanska et al., Ind. Eng. Chem. Res. 58, 21761-21771 (2019)
[3] K. Wysoczanska et al., AICHE J. 66, e16984 (2020)
[4] H. Marques et al., J. Mol. Liq. 348, 118403 (2022)
[5] C. Lopes et al., Fluid Phase Equilib. 567, 113717 (2023)
[6] P. Velho et al., Fluid Phase Equilib. 569, 113766 (2023)

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