

5 Engineering Simulations

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ABSTRACT

Over recent years, ionic liquids have emerged as a class of novel fluids that have inspired the development of a number of new products and processes. The ability to design these materials with specific functionalities and properties means that they are highly relevant to the growing philosophy of chemical-product design. This is particularly appropriate in the context of a chemical industry that is becoming increasingly focussed on small-volume, high-value added products with relatively short times to market. To support such product and process development, a number of tools can be utilised. A key requirement is that the tool can predict the physical properties and activity coefficients of multi-component mixtures and, if required, model the process in which the materials will be used.

Multi-scale simulations that span density functional theory (DFT) to process-engineering computations can address the relevant time and length scales and have increased in usage with the availability of cheap and powerful computers. Herein we will discuss the area of engineering calculations relating to the design of ionic liquid processes, that is, the computational tools that bridge this gap and allow for process simulation tools to utilise and assist in the design of ionic liquids.

It will be shown that, at present, it is possible to use available tools to estimate many important properties of ionic liquids and mixtures containing them with a sufficient level of accuracy for preliminary design and selection.

5.1 INTRODUCTION

Over the last decade or so, ionic liquids have emerged as a class of novel fluids that have inspired researchers to develop new products and processes. The synthesis of these materials leads naturally to approaches being adopted which consider desired functionalities and properties at the outset, and thus ionic liquids are ideally placed to benefit from modern chemical-product design philosophies. Diverse applications spanning sensors, thermal fluids, energetic materials, ion propulsion, embalming fluids, and many more have all led to specific products in recent years. At the larger scale, their utilisation within full and pilot scale industrial processes has also been realised. Here again, success has relied on either the phase behaviour or catalytic properties of the ionic liquids generated or used, thus demonstrating the importance of specific and desired physical or chemical properties.

The ability to design ionic liquids with specific functionalities is one of the greatest attractions, particularly when combined with other well-publicised properties such as significantly lower vapour pressures when compared to molecular counterparts. While such designer functionalities are not limited to the field of ionic liquids, these materials have arguably exemplified the modern approach to chemical-product design to a greater extent than any other recent technology. Sustained growth in ionic liquids research is therefore likely to continue for some time, particularly given that this area has coincided with a marked shift within a chemical industry that is now increasingly focussing on small-volume, high-value added products as opposed to bulk low-value products.

To support the industrial design process, “conceptual” or “process synthesis” tools are increasingly used. Such tools offer users a method of evaluating large numbers of potential routes to the manufacture of a specific product using a combination of experimental and mathematical analyses. Typically, these tools have been applied to the design of continuous processes by combining knowledge of the necessary design parameters, that is, kinetics for reaction, activity coefficients for distillation, and so on, with accurate data on the physical properties of the streams involved and how these change with temperature, pressure, and composition. These models can subsequently be used to theoretically test different designs and maximise efficiency of a single unit or the whole plant. Increasingly important is the use of such tools for the design of energy recycle and efficiency systems, and for the consideration of environmental impact. Here, the steady-state behaviour inherent to continuous processes is beneficial to developing the mathematical tools needed to both select and then optimise a process design or flowsheet. Flowsheet simulations themselves have their origins in a number of published papers relating to unit operation models in the 1950s [1]. These individual models (i.e., distillation, mixing) were then combined together into full flowsheet programs in the 1960s. This was obviously assisted by the evolution of computer technology and the increasing speed and capacity of these machines for handling relatively

large and integrated computations. Over time, these advances in terms of computational power, together with increased availability and enhanced program–user interface interaction, have allowed such tools to be used more than ever in process evaluation, and as such they have become part of typical undergraduate chemical engineering programmes.

In one of our early publications, which considered the engineering of ionic liquids, we highlighted that efficient process design necessitated a complete understanding of the behaviour of these materials under operating conditions [2]. At the time, important physical properties such as viscosity, density, heat capacity, and surface tension, which are necessary for inclusion into design equations for pumping systems, heat exchangers, and so on, were relatively scarce. The commonly available tools used to predict missing physical properties had of course been developed for molecular compounds, but not for ionic liquids. These models thus tended to require information such as the critical temperature and pressure, that is, properties that do not apply to ionic liquids but that nonetheless were subsequently calculated for ionic liquids [3–5]. Similarly, methods for predicting physical properties like surface tension, density, heat capacity, and so on using group contribution methods were simply not available due to a lack of published data, and again standard approaches developed for molecular fluids failed to account for organic salts and therefore could not be used with any degree of confidence.

Over the past decade, databases have become available, such as IUPAC's ILThermo [6]. Since becoming operational, these databases have collected a significant amount of data including common physical properties and their measurement methods. A particular advantage of such repositories is that they have facilitated research into the development of predictive tools to generate group contribution parameters, and other similar structure–property relationships, for these novel fluids. The recent growth in this area has also been recognised within this book, as a number of chapters relate to physical properties of ionic liquids.

In addition to their potential use as solvents or catalysts in large processes, it is important to remember that ionic liquids are increasingly finding application as products in their own right. This area commonly referred to as “product design” is rapidly growing within chemical engineering as a result of the increased importance of developing new and novel products. Here, important objectives are to match the market needs to identified chemicals and/or their mixtures and to quickly evaluate key economic, market, and process design issues in order to support decisions in the early stages of development. As opposed to process design, major objectives are often time-to-market and performance of the required functionality. Further complications arise from the fact that the processes used in their manufacture are likely to be batch and, here, obtaining all the required design information is time-consuming (relative to time-to-market) and costly, and thus uneconomical, particularly where the modelling is further complicated by the inherent nature of the non-steady-state processes, thus leading to challenging design problems. While

“hardware” tools such as modular engineering and micro-fabricated devices are increasingly being used to help to bridge the gap between batch and continuous processes, thus maintaining the main advantages of both, “software” tools have also advanced considerably. Therefore, in addition to device manufacture, there has been a significant growth in advanced computational tools used to aid the development of products and processes for the specialty chemical, pharmaceutical, and microstructured product sectors.

It is clear from the foregoing discussion that the engineering and design tools useful for the various development stages cover a very broad spectrum. Hence an important question here is “What in fact are engineering computations for ionic liquids?” Given the broad range of computational tools used in modern approaches to the engineering of products and processes, there would appear to be no one specific answer to this question. Indeed, Grossmann et al. [7] argued that process design and product design formally belong to the wide body of knowledge known as process systems engineering (PSE). As the computational tools have developed over recent years, so too has the scope of PSE, which has now expanded from the microscopic (molecules) to the macroscopic (process plant). A common way of representing such a multi-scale engineering approach is given in Figure 5.1. Traditional viewpoints would suggest that ionic liquids engineering calculations should specifically focus on problems relating to the design of larger plant with length scales in the order of kilometres and timescales in the order of years. However multi-scale approaches including ionic liquids, such as that shown in Figure 5.1, are now beginning to appear in the literature. One recent example is that by Tian et al. [8], where a multi-scale simulation method was proposed to enable screening of ionic liquids as

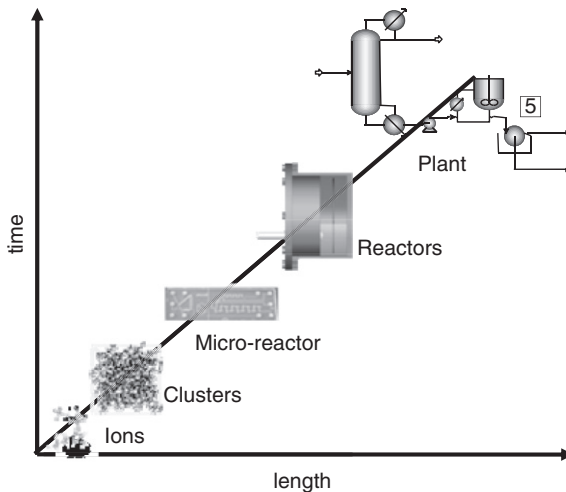


Figure 5.1 A multi-scale modelling approach to engineering computations using ionic liquids.

entrainers for the extractive distillation step in 1,3-butadiene production. Here, the specific term “multi-scale” was adopted, whereas others such as Brennecke et al., who had previously combined molecular simulation, experimental data, and process simulation in an effort to evaluate ionic liquids for gas separations, applied these principles but did not specifically refer to them [9, 10].

For product design applications, there is an obvious attraction towards the molecular level, which has promoted the creation of the area known as computer-aided design modelling (CADM). While this again is not specific to ionic liquids, it is a rapidly growing area and one which should significantly enhance ionic liquid design in the coming years. At the other end of this scale are modern process simulation packages, as discussed previously.

Herein we will focus on the engineering calculations relating to the design of industrial processes, that is, the computational tools that bridge this gap, and allow for process simulation tools to utilise ionic liquids. As will be shown, this can and does include aspects of CADM, as already demonstrated by Tian and Brennecke earlier.

5.2 ENGINEERING COMPUTATIONS FOR PROCESS DESIGN USING IONIC LIQUIDS

Process design itself is often described in the form of an “onion” diagram, as shown in Figure 5.2. Here the reactor forms the core of the process, with the separation and recycle systems being designed around the requirements of the reactor. Then, the heat integration recovery and waste treatment processes are included until the whole process is described. A similar approach can be used

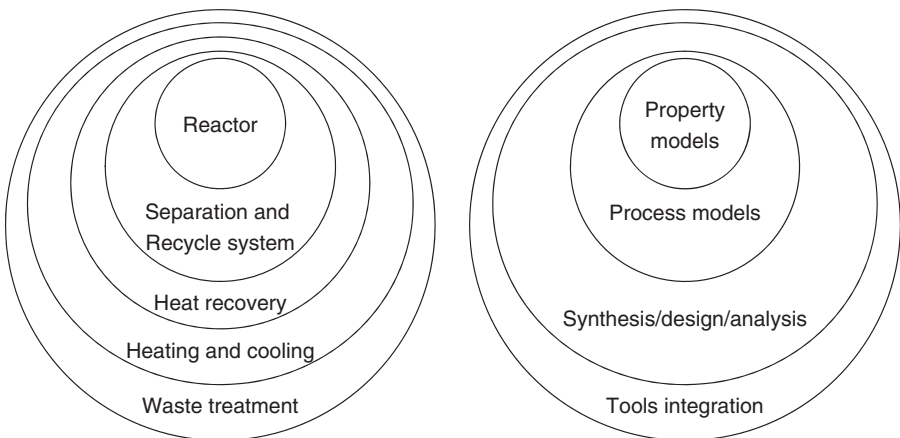


Figure 5.2 Onion diagrams for process design in terms of unit operations (left) and calculation (right).

to describe the engineering computations used to support the design process. In this case, property models represent the core. Using these, the various unit operations can be designed based on their individual mathematical descriptions. As discussed earlier, many commercial flowsheeting software packages, such as ProSim, Pro/II, CHEMCAD, gProms, and Aspen Plus, include unit operation models of varying complexity and rigour, and give users the ability to link them together to form a complete process description.

It should be obvious that the validity of the simulation depends on the accuracy of the property correlation in describing the phase behaviour and properties of the mixture under the given process conditions, that is, temperature and pressure. Within a process, these conditions can vary widely and range from cryogenic to hundreds of degrees centigrade, and from vacuum to hundreds of bars, respectively. In terms of the general structure of algorithms for solving the equipment models and thermophysical properties correlation, several techniques, such as sequential-based modular, simultaneous-based modular, or equation-based techniques, have been developed to optimise and reduce the time required to solve the whole flowsheet of equipment. A review of these techniques has been published previously by Perkins [11].

Property models, which are at the heart of process design calculations and are specific to a discussion on ionic liquids, can be categorised into two areas: (1) those that can be used to correlate physical properties (i.e., heat capacity, thermal conductivity, viscosity, etc.) with temperature and others, and (2) thermodynamic models used for determining the state of matter under processing conditions (equations of state [EoS]) and the interactions between molecules (i.e., activity). As stated earlier, thermophysical properties have been discussed and reviewed elsewhere, and so the focus here will be on thermodynamic models, particularly those related to separation processes involving ionic liquids.

5.3 THERMODYNAMIC MODELS FOR IONIC LIQUIDS

In order to address the needs of engineers when undertaking product and process design of systems based on ionic liquids, investigation and measurement of phase equilibria and related thermophysical properties are essential. However, as previously discussed, experimental data collection for the desired range of temperature, pressure, and composition are both expensive and time-consuming. Therefore, thermodynamic modelling is a necessary step in determining the optimum operating conditions, process performance, and equipment sizing for a given unit operation. While considerable advancement has been achieved in estimating thermodynamic behaviour from simple molecular descriptors, this has not yet reached a sufficiently high accuracy to be used in isolation. Therefore, the application of any thermodynamic model to a particular system will require some experimental data in order to enhance and validate the applicability of the chosen model.

Studies of such models for ionic liquid-based systems began approximately a decade ago during investigation of aromatic extraction from mixtures of paraffin and aromatics using 1-ethyl-3-methylimidazolium triiodide, $[\text{C}_2\text{mim}][\text{I}_3]$, or 1-butyl-3-methylimidazolium triiodide, $[\text{C}_4\text{mim}][\text{I}_3]$. The non-random two liquid (NRTL) activity coefficient model [12] was chosen, as other Gibbs excess (G^E) models for liquid–liquid equilibria (LLE) such as van Laar and Wilson were unsuitable due to the non-ideality of this particular system. Popular alternatives, such as UNIQUAC and UNIFAC, required molecular parameters which were not available at that time. For similar reasons, EoS methods could not be evaluated due to a lack of critical properties, including acentric factors, dipole moment, polarisability, and so on. Furthermore, quantum chemical calculations, which are now increasingly common, were not sufficiently advanced in order to predict such behaviour for ionic liquid systems. However, as previously discussed, a significant increase in experimental data has occurred over the last decade, allowing for the correlation, modelling, and subsequent prediction of ionic liquid-based systems using a variety of the aforementioned models. Thus, the barriers derived from a lack of experimental data needed to determine group parameters, for example, and to verify such models, have diminished accordingly. Herein we will attempt to review recent progress in this area, and to aid this discussion the various models will be categorised into one of the following groups:

- Gibbs excess models
- EoS
- quantum chemical calculations

5.3.1 Gibbs Excess G^E Models

After the initial work of Selvan et al. [12], Domanska and coworkers [13, 14] measured and correlated binary solid–liquid equilibrium (SLE) systems containing ionic liquids with alcohols using three different G^E models (i.e., Wilson, modified NRTL [15], and UNIQUAC ASM [16]). The resulting correlation yielded standard mean deviations ranging from 0.7 to 4.77 when compared to the experimental data. The same group subsequently modelled the binary SLE and LLE systems of $[\text{C}_2\text{mim}][\text{PF}_6]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ with aromatic hydrocarbons using both UNIQUAC and NRTL with a much improved deviation of around 0.4 [17]. Since then measurements and correlations utilising the Wilson, NRTL, and UNIQUAC methods have been performed; however, these focus mainly on binary solid–liquid mixtures containing ionic liquids with another compound [18–47]. Similar work was carried out by Shiflett et al. for binary gas–ionic liquid systems [48–51] and LLE [52–57], respectively, and the results were again all correlated using the NRTL method. Ternary systems (LLE) have also been modelled using this method by Arce et al. [58–75], Pereira et al. [76–84], Gonzalez et al. [85–91], and Letcher et al. [92–94], where prediction of the ternary phase diagram tie lines and binodal curve have been

demonstrated. These correlated phase equilibria included azeotropic mixtures, in which azeotropic (alkane + alcohol), (ketone + alcohol), (alkane + ester), (alcohol + ester) mixtures are separated using an ionic liquid extraction solvent [76, 78–81]. Overall, the predictions were adequate, although sometimes poor correlations were obtained when compared to experimental results depending on the systems studied. This poor performance of the NRTL equation was found in cases that contained high concentrations of the solute, such as thiophene, as reported by Alonso et al. [62].

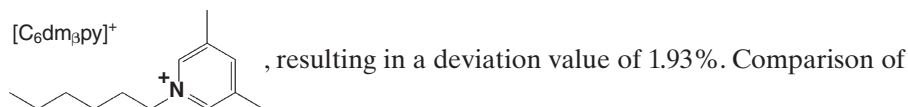
Modification of the NRTL method to model systems containing electrolytes was proposed by Chen et al. [95] in 1982. This model was initially developed for describing systems containing water and free ions, that is, electrolyte solutions, and was described as the electrolyte NRTL (e-NRTL) model. In essence, this model attempts to take into account long-range interaction between ions (Coulombic interaction) as well as the short-range interactions between ion–molecule (electrostatic forces) and between molecule–molecule (dipole–dipole, induced dipole, van der Waals forces). From this description, it would appear that the e-NRTL model should be more representative of ionic liquids, and because of this it was applied to mixtures of ionic liquid and water by Belvèze et al. [96] and Chapeaux et al. [97], respectively. In Belvèze et al. [96], binary mixtures of quaternary ammonium ionic liquid using various anions at low concentrations with water were modelled for activity coefficient at 25°C. In this model, and due to the low ionic liquid concentration in the water, the ionic liquid was assumed to be completely dissociated within the water phase. From the resulting correlation, it was shown that the e-NRTL works very well for modelling the activity coefficients of this ionic liquid in water. However, limitations of this simple model appear at higher concentrations and for highly branched compounds, where the assumptions of complete dissociation no longer hold true. Hence, this model is unable to describe the effect of incomplete dissociation as well as micelle formation. Other works on e-NRTL modelling with ionic liquids to investigate salting out effects of the ionic liquid in a molecular solvent as well as its effect on azeotropic breaking have been reported by Orchillés et al. [98–104] for vapour–liquid equilibrium (VLE) and LLE systems, respectively.

Accepting the limitations of the e-NRTL model, another approach for predicting LLE of ionic liquids and mixed solvent systems was developed by Simoni et al. [105, 106]. Known as the asymmetric framework method, it is designed such that it calculates the ionic liquid-rich phase and high-average-dielectric-constant solvent-rich phase compositions separately using NRTL and e-NRTL methods, respectively. The theoretical assumption behind this work is that an ionic liquid associates and dissociates to different degrees depending on the phase in which it is dissolved; thus, different models are applied to each phase. One phase is characterised by a high concentration of ionic liquid, and when in a mixed solvent with a low dielectric constant it is assumed to have completely associated ions, that is, ion pairs (molecular-like), whereas the other phase that contains a low concentration of ionic liquid and

in a mixed solvent of high dielectric constant is assumed to have complete dissociation of the ions. Although not extensively applied to date, the asymmetric framework appears to only work well in predicting LLE of ternary systems involving an aqueous phase that is dilute in ionic liquid, which is of course the intended application of this method.

More recently, another type of NRTL modification was proposed by Chen and Song [107] by introducing four different “conceptual” segments that are broadly characterised by various surface interaction characteristics of the molecules which measures the hydrophobicity, hydrophilicity, polarity, and solvation strength of the molecular surface areas known as molecular descriptors. This segmented calculation of the residual term of the activity coefficients is termed the NRTL segmented activity coefficients (NRTL-SACs) model. In a subsequent paper, Chen et al. [108] applied the NRTL-SAC method to ionic liquid systems by firstly correlating the infinite-dilution activity coefficients for organic solvents in ionic liquids and then using the resulting molecular descriptors to predict their phase behaviour in various mixtures. This method was found to predict VLE behaviour with comparable results to that obtained from Wilson, NRTL, and UNIQUAC [109], although it was less successful in predicting LLE phase behaviour. At present, the segments proposed in the NRTL-SAC method appear to overpredict the activity coefficients of alkylbenzenes with ionic liquids as well as alcohol, in this case 2-propanol, in ionic liquids with higher alkyl chain lengths. One particular advantage of using the NRTL-SAC method is that the predictions are based on pure component ionic liquid molecular descriptors rather than the binary interaction parameters needed for other G^E models such as Wilson, NRTL, and UNIQUAC. This is a significant advantage over these other models as it reduces the amount of experimental data needed to describe a given ionic liquid system. However, NRTL-SAC is more numerically intensive and complex when compared to these alternative methods and it is unlikely that the descriptors are sufficiently broad enough at present to correctly describe ionic liquid behaviour in all situations.

Several other published works have used the UNIQUAC method to correlate binary and ternary systems containing ionic liquids [110–112]. Typically, the values R_k (van der Waals volume) and Q_k (van der Waals surface area) are estimated from the Bondi method [113] as described by Kato et al. [114]. Banerjee et al. [115], however, used the polarisable continuum model (PCM) to generate R_k and Q_k , giving a 40% improvement in the root mean square deviation (RMSD) over NRTL. Santiago et al. [111, 112] meanwhile utilised quantum chemical calculations performed by the Gaussian 03 and GAMESS 7.1 packages, which included optimisation of a component’s structure via DFT. The generated R_k and Q_k parameters were used in the UNIQUAC correlation



NRTL and UNIQUAC methods in correlating similar measured systems has been performed by a number of groups such as Pereiro et al. [116–118], Arce et al. [119–123], and Garcia et al. [124, 125]. In general, UNIQUAC was found to give a better correlation when compared to NRTL. For example, in Alonso et al. [119], the RMSD of the residual function was found to be 8.2 and 1.4 for NRTL and UNIQUAC, respectively, when correlating ternary systems containing ($[C_8\text{mim}][\text{NTf}_2]$ + thiophene + toluene). Similar studies by Arce et al. [122], using $[C_6\text{dm}_3\text{py}][\text{NTf}_2]$ to extract thiophene from mixtures containing toluene or heptane or trimethylpentane, respectively, also found that the use of the UNIQUAC model resulted in lower deviations than that given by NRTL. Studies by Pereiro et al. [116] on binary systems containing $[C_n\text{mim}][\text{PF}_6]$ with 1-propanol, 1-butanol, or 1-pentanol at various temperatures indicated that both NRTL and UNIQUAC equations show a satisfactory fit to the experimental data. Further comparison of the Wilson, NRTL, and UNIQUAC methods have been reported by Domańska et al. [40] and Doker et al. [109]. The latter paper used these methods to correlate the binary VLE of $[C_2\text{mim}][\text{NTf}_2]$ and $[C_4\text{mim}][\text{NTf}_2]$ with propanone, 2-propanol, or water, respectively, giving average deviations of 3.92%, 1.45%, and 1.53%. As expected, the poor correlation of the Wilson equation for the binary system is due to its inability to describe the miscibility gap of the water–ionic liquid system, whereas good agreement was found for both NRTL and UNIQUAC. Using the same G^E model parameters, predictions were made and compared with experimental data sets with reported errors when using Wilson, NRTL, and UNIQUAC of 5.61%, 7.22%, and 5.02%, respectively, which shows that the G^E models could provide acceptable results for binary and ternary phase equilibria at typically low pressures and mild temperatures.

Predictive versions of this G^E model such as UNIFAC have long been used to estimate unmeasured systems through prior determination of the binary interaction parameters of the respective functional groups. Until recently, functional group parameters for ionic liquids were not available in published databases; however, as experimental data have increased, the calculation of these parameters has since been made possible. Here both Wang et al. [126] and Lei et al. [127] have shown the applicability of the UNIFAC model to predict thermodynamic properties and phase behaviour of systems containing ionic liquid. In the paper by Wang et al. [126], the ionic liquids are segmented into several neutral functional groups as suggested by Kim et al. [128], in which the bulk cation and anion of the ionic liquid are treated as one main group. However, closely adjacent atoms or groups which can be subjected to electrophilic effects by strong electronegative atoms or electrophilic groups such as nitrogen, oxygen, hydroxyl, and carbonyl are most likely not separable. This thus leads to two alternative approaches which either include or exclude the adjacent groups connected to the electronegative atom of the cation as part of the main group of the ionic liquid. In their work, the resulting binary parameters were correlated from measured data of infinite-dilution activity coefficient of several ionic liquids with molecular solutes such as alkanes, alkenes,

aromatics, alcohols, ketones, and water and used to predict the vapour pressure of binary mixtures containing ionic liquid at various temperatures with an RMSD of less than 4.2%. Similarly, results reported by Lei et al. [127] also showed that after further extending the group parameters for the UNIFAC model to include other ionic liquid main groups beyond the reported imidazolium-based ionic liquids with the $[\text{NTf}_2]^-$ anion, prediction of VLE for a system with ionic liquid could be performed with reasonable accuracy.

However, a limitation was found for predicting non-polar solute–ionic liquid systems due to the UNIFAC model slightly overpredicting the homogeneity of the liquid phase when liquid–liquid demixing should have taken place. Work by Alevizou et al. [129] was based on treating the imidazolium and hexafluorophosphate group as separate entities each having its individual value of R_k , Q_k , and group binary parameters determined simultaneously by fitting binary LLE and infinite-dilution activity coefficient experimental data. This was then further tested to predict ternary LLE of systems containing $[\text{C}_n\text{mim}][\text{PF}_6]$ with alkanes, alcohols, and water, respectively. In this work, the UNIFAC model successfully predicted the phase behaviour of the ternary systems but with considerable underestimation for the size of the biphasic region for the longer alkyl chain length of the imidazolium cation (i.e., $[\text{C}_6\text{mim}][\text{PF}_6]$ and $[\text{C}_8\text{mim}][\text{PF}_6]$). It is also worth noting that the original UNIFAC model was adopted in all of the works mentioned earlier [126, 127, 129]. An augmented UNIFAC (Do) model was proposed in 1987 by Gmehling and coworkers [130–134], which introduced modifications to the combinatorial part by including temperature-dependent group interaction parameters simultaneously calculated for VLE, LLE, enthalpy of mixing (H^E), and gamma infinity (γ^∞) data. Naturally, this requires a massive databank of phase behaviour measurements over a wide temperature range. Despite this requirement, application of the modified UNIFAC (Do) model to systems containing ionic liquid has been reported [135–143], in which, for the most part, the modified UNIFAC results in better agreement with experimental data especially for the calculation of H^E and γ^∞ due to the temperature-dependent parameters. In one of the group's earliest papers relating to ionic liquids, Kato and Gmehling [135] described the main imidazolium cation and bis((trifluoromethyl)sulfonyl)amide anion as separate individual groups, where the relative van der Waals volumes (R_k) and surface areas (Q_k) were obtained using the Bondi method [113]. As before, Santiago et al. [144] proposed using quantum chemical calculation through molecular geometry optimisation via DFT, and later using the PCM model for the area and volume calculation.

A comparison of several different G^E models for modelling the extraction of alcohols from water using $[\text{C}_6\text{mim}][\text{NTf}_2]$ through the development of ternary phase diagrams has been reported by Chapeaux et al. [145]. In this work, four different G^E models (consisting of NRTL, e-NRTL, UNIQUAC, and UNIFAC) were used to predict the behaviour of ternary LLE systems of types I and II, respectively, based solely on parameters determined from binary data measurements. UNIQUAC was found to be the best model for predicting

the type I system (although NRTL provided the most accurate tie lines in this case), and e-NRTL and UNIQUAC were the better models for predicting the type II system. Similar comparison work was also reported by Simoni et al. [146] for predicting ternary systems of (ionic liquid + water + alcohol), (ionic liquid + aromatic + aliphatic), (ionic liquid + ether + alcohol), and (ionic liquid + ether + water) systems, respectively.

5.3.2 EoS Models

In 2003, Shariati and Peters [147] reported one of the first EoS models used for correlating the VLE of systems containing $[\text{C}_2\text{mim}][\text{PF}_6]$ and trifluoromethane (CHF_3). This work used the Peng–Robinson (PR) EoS at temperatures and pressures ranging from 309.3 to 367.5 K and 1.6 to 51.6 MPa, respectively. Similar work by Liu et al. [148] reported the VLE modelling of a ternary system consisting of CO_2 , $[\text{C}_4\text{mim}][\text{PF}_6]$, and methanol mixtures at elevated pressures. The corresponding solubility and viscosity of the liquid phases at equilibrium conditions were also modelled using the same EoS method. Carvalho and coworkers [149–151], in their series of published works on high-pressure carbon dioxide phase behaviour in ionic liquids, also used the PR EoS coupled with the Wong–Sandler mixing rules. Here the UNIQUAC model was used for calculating the activity coefficients and to describe Henry's constants of CO_2 with imidazolium-based and phosphonium-based ionic liquids, respectively, at temperatures of up to 363 K and pressure of up to 74 MPa. Good agreement was found with the experimental data. Several other authors have also reported the application of the PR EoS to describe binary VLE for systems containing ionic liquids with refrigerant gasses [152], compressed CO_2 [153], supercritical fluids, and hydrocarbons [154], respectively. Trindade et al. [155] further studied the applicability of PR EoS combined with the Mathias–Klotz–Prausnitz (MKP) mixing rule to correlate the binary LLE of imidazolium-based ionic liquids $[\text{C}_2\text{mim}][\text{NTf}_2]$, $[\text{C}_{10}\text{mim}][\text{NTf}_2]$, and $[\text{C}_2\text{mim}][\text{OTf}]$ with 1-propanol, 1,2-propanediol, 1,3-propanediol, and glycerol (1,2,3-propanetriol), respectively. In this work, satisfactory correlation was achieved with most of the systems studied, except in the case of 1,3-propanediol.

Recently, Arce et al. [156] used a modified version of the PR EoS called PR + Stryjek–Vera (PRSV) EoS model to describe the phase equilibria of 17 binary gas and ionic liquid systems at high pressures, which achieved satisfactory results. In this work, comparison of two different mixing rules based on phi–phi (van der Waals) and gamma–phi (Wong–Sandler + Van Laar) approaches showed comparable deviations to the experimental results, with the phi–phi approach requiring less computational time in comparison with gamma–phi. Meanwhile, Ren et al. [157] studied the effect of cation alkyl chain length of imidazolium-based ionic liquids with the $[\text{NTf}_2]^-$ anion on CO_2 solubility at several temperatures and pressures of up to 25 MPa, and modelled these using the PR EoS in combination with the van der Waals two-parameter mixing rule. In this work, and at temperatures below the CO_2 critical point,

that is, 304 K, the various multiphase equilibria, viz. VLE, LLE, and VLLE were satisfactorily modelled by the PR EoS within the experimental pressure range. However, above the correlated pressure, that is, 25 MPa, extrapolation of the model predicts physically unrealistic dew points, ionic liquid solubility in the liquid CO₂, and mixture critical point.

Shiflett and Yokozeki measured considerable amounts of solubility data for various gases in a variety of ionic liquids over a wide range of pressures, which were then modelled using a modified Redlich–Kwong (RK) EoS [158–169].* In their series of published works, and from the measured P - T - x data of gas solubility in ionic liquid, excess properties such as enthalpy (H^E), entropy (S^E), and Gibbs energy (G^E) of the mixtures could be calculated using the modified RK EoS correlation. This can be used to imply the strength of attractive interaction between the gas and ionic liquid through the positive or negative values of the excess properties. For example, in one paper [162], very strong attractive intermolecular interactions such as hydrogen bonding have been suggested to exist in the studied binary mixture of ammonia and ionic liquid which is deduced from the highly negative calculated values of H^E and G^E . This is in accordance with experimental observations of high ammonia solubility in ionic liquids as well as the homogenous nature of the mixture. In all of these works which involved classical cubic EoS, for example, PR-EoS or RK-EoS, ionic liquids are considered neutral clusters of ions. In terms of calculation, the vapour phase was assumed to contain a negligible amount of ionic liquid, allowing the fugacity coefficient of the components in the vapour phase to be calculated. This then utilises the K -value (distribution coefficient) to determine the fugacity coefficients in the liquid phase and eventually the binary interaction parameters of the ionic liquid with the individual component at the respective temperature. The chosen EoS methods were satisfactory in terms of describing the experimental bubble point, but were only able to qualitatively predict the solubility of ionic liquid in the supercritical solvent-rich phase due to the very low mole fraction, particularly near the critical region.

In order to better describe the solubility of gases such as CO₂ in ionic liquids at high pressure, molecular-based EoSs were applied to characterise the interaction of these gases with respective ionic liquids through several theoretical models for the mixture. Here these EoSs are based solely on statistical mechanics that allow physical interpretation of the effect of molecular structure on thermodynamic properties to be classified and quantified. Using a truncated perturbed chain polar statistical associating fluid theory (tPC-PSAFT EoS), Kroon et al. [170] reported the correlation and prediction of CO₂ phase behaviour in various imidazolium-based ionic liquids with different cation alkyl chain lengths and different anions at pressures up to 100 MPa. This work is based on a theory expressed through the residual Helmholtz energy where

* See also Shiflett, M.B. and Yokozeki, A., Phase behaviour of gases in ionic liquids, in *Ionic Liquids UnCOILed: Critical Expert Overviews*, eds. N.V. Plechkova and K.R. Seddon (Wiley, Hoboken, New Jersey, 2012), pp. 349–398.

molecular dipolar interactions are described between ionic liquid molecules, which are themselves assumed to be neutral ion pairs. Between CO_2 molecules quadrupolar interactions are used, and interactions between the ionic liquid and CO_2 molecules are described by Lewis acid–base-type associations. Overall, good agreement with VLE experimental data was obtained for all cases. Karakatsani et al. [171, 172] later on re-estimated the parameters of tPC-PSAFT for imidazolium-based ionic liquid by fitting available density data over a wide range of temperature, which resulted in a much lower and improved values of binary interaction parameters for the gas and ionic liquid [170].

Andreu and Vega [173] reported an application of another type of SAFT EoS, called soft-SAFT, to model CO_2 solubility in $[\text{C}_n\text{mim}][\text{BF}_4]$ and $[\text{C}_n\text{mim}][\text{PF}_6]$ at various temperatures and pressures of up to 90 MPa. In this work, interactions are categorised into four classifications: a reference term that was based on Lennard-Jones spherical fluids, chain formation, the association, and the polar interaction of molecules. Molecular parameters and association parameters of the pure components that are required prior to applying the EoS to a given mixture were obtained by initially fitting the parameters to experimental density data. The soft-SAFT EoS qualitatively described the solubility of CO_2 in ionic liquids although successful parameterisation requires accurate models of pure ionic liquids based on molecular simulation. Although the equation is simple, the mathematical complexity which requires high numbers of different parameters in solving could be a significant hindrance for wider implementation. Andreu and Vega [174] later applied the soft-SAFT EoS to model solubility of CO_2 as well as other gases such as H_2 and xenon in $[\text{C}_n\text{mim}][\text{NTf}_2]$ at several different temperatures and pressure of up to 100 MPa. More recently, Vega et al. [175] continued to extend the soft-SAFT EoS for modelling the solubility of BF_3 in $[\text{C}_n\text{mim}][\text{BF}_4]$ at various temperatures and pressures. However, while previous soft-SAFT models of CO_2 solubility in ionic liquids did not require cross-association interaction [173, 174], this is not the case with BF_3 due to the 1:1 weak interaction between the gas and ionic liquid “molecule.” Hence, explicit cross-association interactions between the two components are required, resulting in a higher number of parameters for the soft-SAFT model.

Other groups such as Wang et al. [176] used the square-well chain-fluid EoS (SWCF-EoS) to model the P - V - T behaviour of pure ionic liquids and their respective phase behaviour with gases by representing ionic liquids as “diblock compounds” with the cation alkyl chain length group as one block and the imidazolium ring–anion pair as the other. Correlation of VLE for 22 binary systems containing imidazolium-based ionic liquids and solvents provided satisfactory results with an average deviation of 5.38%. Li et al. [177] further refined this EoS by introducing variable interaction ranges for the disperse contribution of the Helmholtz function as well as treating the chain formation contribution separately into respective hard spheres and square-well potentials. From this treatment, the molecular parameters were obtained from the

correlation of the experimental density data of pure ionic liquids, which were then coupled with the fluid mixture rule and temperature-independent binary interaction parameters obtained from experimental solubility data, thus enabling calculation of the properties of ionic liquid mixtures. Comparison between the calculated results and the experimental data showed satisfactory results for data at low pressures. Other forms of the EoS based on chemical association theory using lattice-fluid model (LF-EoS) were extended to model the ionic liquid systems. Initially proposed by Yang et al. [178], these combine computer simulation results with statistical mechanics to obtain expression for the Helmholtz energy of mixing. In this work, infinite-dilution activity coefficients, binary VLE, and LLE of systems containing ionic liquids were correlated satisfactorily. However, due to the close-packed characteristics of the proposed model in this work, it was unable to calculate the effect of pressure on phase behaviour. In order to overcome this limitation and enable the calculation of P - V - T properties and phase equilibria for systems containing ionic liquid, a modification was proposed by Xu et al. [179], which introduced holes into the lattice structure. In addition, a new parameter determined from Monte Carlo simulation data was introduced to characterise the long-range correlations beyond the close contact pairs. Using this model, the P - V - T properties, VLE, and LLE of binary systems containing ionic liquids were satisfactorily described. Here correlation of binodal curves for ternary LLE were obtained through determination of component-specific binary interaction parameters.

Approaches for using group contribution EoS (GC-EoS) in predicting phase behaviour of systems containing ionic liquids have been developed and proposed by several groups in an attempt to predict solubility of gases in ionic liquids at high pressure. Kim et al. [128] used a GC non-random lattice-fluid EoS (GCNRLF-EoS) to predict solubilities of CO_2 in six methylimidazolium-based ionic liquids at pressures of up to 1 MPa. Each ionic liquid was segmented into functional groups where binary interaction parameters between the groups were determined from fitting experimental data. In general, the predicted values of CO_2 solubility in ionic liquids were in good agreement with the experimental data; however, no prediction for higher pressures (>1 MPa) is reported. Breure et al. [180] applied a GC-EoS, which was originally proposed by Skjold-Jørgensen [181, 182] in the 1980s to calculate the VLE of non-ideal mixtures for pressures of up to 30 MPa. This GC-EoS is based on a generalised van der Waals function in combination with a local composition principle, and was expressed in terms of residual Helmholtz energy, which took into account the attractive term and free volume term, respectively. From the determined pure group constants, pure group attractive energy parameters, as well as group-group binary interaction parameters, were found. At pressures of up to 20 MPa, the predicted results were in very good agreement with experimental data, with absolute average deviations ranging from 1% to 4%, and for pressures as high as 100 MPa, predictions were qualitatively in good agreement with the experimental data. Martin et al. [183] applied a similar approach to correlate the phase behaviour of several gases (CO_2 , O_2 , or SO_2)

in ionic liquids with the $[\text{NTf}_2]^-$ anion and cations of the families 1-alkyl-2,3-dimethylimidazolium, 1-alkyl-1-methyl-pyrrolidinium, and 1-alkyl-3-methylpyridinium. The newly obtained parameters were later used to predict the VLE of other ionic liquids belonging to the same families with the gases mentioned earlier. This GC EoS was able to correctly predict the trend of phase behaviour with respect to the experimental results; however, deviation was higher for data at low pressures and temperatures. Bermejo et al. [184] later extended the GC EoS to predict the binary system of CO_2 with imidazolium-based ionic liquids employing the nitrate anion for pressures of up to 12 MPa with an average deviation of 4.75%. However, adjustment of the ionic liquid critical diameters was necessary in order to achieve a good correlation.

5.3.3 Quantum Chemical Calculations

A more *a priori* effort was made by Diedenhofen et al. [185] through the application of **C**ONductor-like**S**creening**M**ODEL of Real Solvents (COSMO-RS) in predicting the infinite-dilution activity coefficients of 38 compounds with three different ionic liquids. In this work, quantum chemical calculations were initially performed by parameterisation of the compound structure through an *ab initio* calculation, which generates a surface charge density (σ) profile of the individual compound. This was then followed by a COSMO-RS thermodynamic model which utilised these sigma profiles to describe the interaction of the compounds within the mixture and, hence, the respective chemical potential. This departure of the component's chemical potential in the mixture from its pure compound chemical potential then allows thermodynamic properties such as activity coefficient to be calculated. This *a priori* thermodynamic calculation of properties for ionic liquids obtained simply from the chemical structures was able to provide a predictive tool with comparable accuracy to that observed for normal organic solvents. Jork et al. [186] further discussed the use of COSMO-RS as a tool for pre-selection of ionic liquids as entrainers through identification of favourable structural variations of the ionic liquids. Through the activity coefficient calculation, variations in the predicted results were identified due to the different conformations of the volatile components and ionic liquids, respectively. In the case of VLE systems containing ionic liquids, the effect of solvent conformations increased with the polarity of the solvents, whereas the ionic liquid conformer effect on VLE was secondary; hence, modelling the VLE system of ionic liquid and polar solvent requires the consideration of all solvent conformers within the homogenous liquid phase. Conversely, prediction of LLE for systems containing ionic liquids using COSMO-RS is significantly dependent on the ionic liquid conformers, especially for the composition of the ionic liquid-rich phase. Overall, qualitative agreement of the predicted solubility was obtained with experimental results with increased deviation as the concentration of solvent increases in the ionic liquid-rich phase. This is due to the inability of COSMO-RS to accurately describe the long-range interactions (electrostatic contribution).

Banerjee and coworkers used COSMO-RS to predict binary VLE of systems containing five different imidazolium-based ionic liquids with various solvents, in which the RMSD for pressure prediction was 6% in comparison with the Wilson, NRTL, and UNIQUAC models, which resulted in RMSDs of 4%, 1.45%, and 3.13%, respectively [187]. An extension of similar work for LLE was performed by the same group for ternary systems containing ionic liquids, ethanol, and alkenes [188]. In this work, complete dissociation of cation and anion was assumed and conformer correction of the sigma profile of the alkenes was adopted prior to the calculation of tie lines in the ternary system. The effect of this treatment results in the average RMSD improving from 22.6% to 10.6%. Using this dissociating assumption, COSMO-RS was able to qualitatively predict the correct concentration of ethanol in ionic liquid-rich phase. However, this also resulted in the ethanol concentration in alkene-rich phase being poorly predicted especially for the case of high ethanol concentrations in the alkene-rich phase. Preliminary screening of suitable ionic liquids using COSMO-RS for specific applications of ionic liquids in extraction process, such as thiophene from hydrocarbon [189], phenol from aqueous solution [190], and alcohol or tetrahydrofuran in aqueous systems [191], have also been studied by the same group. Freire et al. [192–194], in a series of publications, evaluated the use of COSMO-RS in predicting mutual solubilities of water in ionic liquids, VLE, and LLE of binary mixtures of imidazolium- and pyridinium-based ionic liquids and alcohols, as well as VLE and LLE of binary systems containing ionic liquids and water, respectively. In general, COSMO-RS was able to give a good qualitative prediction of the VLE system in comparison with the experimental data. However, LLE prediction of the system became poorer as the alkyl chain length of the ionic liquid or solvent (i.e., alcohol) increases, or for very small molecules such as methanol [193]. An increase in the deviation for LLE prediction was also observed as the anion hydrophilicity increases [194].

Further comparison of COSMO-RS in predicting VLE and infinite dilution of binary systems containing ionic liquids with the original and modified UNIFAC method have been reported by Kato et al. [135] and Lei et al. [195], respectively. For LLE systems, Sahandzhieva et al. reported a comparison of a COSMO-RS prediction and UNIQUAC correlation for $[C_4mim][PF_6]$ with three different alcohols (ethanol, 1-propanol, and 1-butanol) at several temperatures. Although a better representation of the experimental data was achieved using UNIFAC and UNIQUAC methods, due to the nature of the COSMO-RS method, in that no prior experimental data is necessary, it can be, and has been, used widely as a tool for qualitative prediction and screening of ionic liquid properties and its phase behaviour with other solvents [196].

However, it is worth noting that the COSMO-RS model alone is not sufficient to provide the relationships of fugacity or chemical potential of a component in a phase with the physicochemical properties of that phase, such as caloric properties (e.g., heat capacity) or volumetric properties (e.g., density), which EoS and G^E thermodynamic models can perform.

5.4 CONCLUSIONS

The sections in this chapter have attempted to discuss the various methods used to describe the thermodynamic properties of ionic liquids. As can be seen, no one method has had universal acceptance. This is, of course, unsurprising; no one method has ever been applied to non-ionic liquid systems, and hence process simulators such as Aspen Plus continue to offer a number of different physical property options. In addition to the normal problems with identifying a suitable physical property model, it is worth remembering that ionic liquids do pose some additional complications in that they have properties common to both salts and normal molecular solvents. These materials can dissociate, cluster, exchange with other ions in the system, or interact with other molecules using a variety of methods, and therefore, depending on the system being studied, it may be better to consider the ionic liquid as being composed of individual ions, ion pairs, or ionic liquid clusters. To date, the NRTL group of methods appear to be by far the most applied models for describing ionic liquid VLE and LLE. This is likely due to the fact that this method is relatively robust and easy to use, and has shown success for a wide range of systems. Extensions to this including e-NRTL have been used in an attempt to better describe the dissociation of the ionic liquid in aqueous systems, again with some success particularly for dilute systems in aqueous media. Apart from its wide applicability, the fact that it does not require information on the relative van der Waals volume (R_k) and surface parameters (Q_k), required for other local composition methods such as UNIQUAC and UNIFAC, has also likely contributed to its popularity. More recently, the asymmetric framework method has been used to try and bridge the gap between both these methods, again showing success for those systems to which it is most relevant. In addition, recent attempts to simplify the NRTL method, in terms of the overall number of interaction parameters needed, by using an SAC approach also show promise. This will be especially true if segments can be included which better describe the charged nature of the ionic liquid. EoS models have also been investigated in recent years, spanning well-known correlations such as PR to more elaborate methods such as the GCNRLF-EoS. Again, these have shown some success particularly for gas phase systems. Furthermore, as computational power has increased in recent years, so too has the ability for molecular dynamics and quantum chemical calculations to assist in prediction of phase equilibria. Of the methods discussed within the literature, COSMO-RS has been used by a number of groups with varying success. However, again, an understanding of the actual structure in terms of conformers and so on appears important for correctly defining the relevant phases. This highlights that understanding the physical nature of the ionic liquid and associated molecules is crucially important.

Overall, the area of engineering computations has increased significantly in recent years and currently it is possible to use available tools to estimate the properties of ionic liquids and mixtures containing them with sufficient accu-

racy for preliminary design and selection. Such tools vary in complexity, with most requiring significantly less time and effort than experimentally determining them. Over the coming decade, it is anticipated that multi-scale engineering approaches will be routinely used for the design of ionic liquid systems.

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