# *Chapter 6*

## Summary

In order to select the most suitable IL solvents for separation processes from the enormous number of possibilities (depending on the different kinds of cation and anion combinations), many researchers use CAILD methods to design or screening IL solvents. In **Chapter 1**, the common structure of CAILD methods is summarized, and the related researches are reviewed. It is found that the hazardous potential of ILs to the environment is not taken into consideration in many published papers. In fact, ILs can be released to the environment through industrial wastewater due to their significant solubility in water. Therefore, in order to design environmentally friendly ILs, their toxicity should be considered in CAILD methods and treated as an essential constraint in the design procedure.

The QSPR models in the literature for the prediction of ILs toxicity are always based on complex descriptors such as GATEWAY (GEometry, Topology, and Atom-Weights AssemblY) descriptors, which require specific software. This makes these models hard to be efficiently used in CAILD methods. For the development of an efficient and reliable QSPR model to predict the ILs toxicity (which can be also directly employed by the CAILD methods), in **Chapter 2**, a QSPR model based on the GC-COSMO method is presented. A database containing the toxicity of 127 ILs towards IPC-81 is built and used to develop the linear and nonlinear QSAR models. The descriptor used in this model is derived from the $\sigma$-profile using two segmentation methods. The cross-validation and the external validation confirmed that all the presented models are not overt fitter and reliable. The nonlinear model MLR-2 shows the best performance with $R^2 = 0.975$, MSE $= 0.019$ for the training set, and $R^2 =$

$0.938$, MSE $= 0.037$ for the test set. Based on the proposed toxicity prediction model, three CAILD scenarios are studied in the following chapters.

In **Chapter 3**, a CAILD method is presented to design ILs for the extraction of benzene from its mixture with cyclohexane. The design problem is formulated as an MINLP problem and solved by the BONMIN algorithm. The top five IL candidates with the highest $PI^{\infty}$ and meet all the physical property constraints ($T_m < 298.15$ K, $\eta < 100$ cP, and $\log EC50 > 2$). [$COC_2$MIM][$Tf_2$N] is selected for the experimental validation by LLE, and the corresponding NRTL parameters are regressed. It turns out that [$COC_2$MIM][$Tf_2$N] shows good performance for the extractive separation of benzene/cyclohexane ($S^{\infty} = 23.39$ and $\beta^{\infty} = 2.22$), and the low melting point, viscosity, and toxicity indicating the potential of this IL as an alternative solvent. The results confirmed that the proposed CAILD is a reliable and efficient method to design ILs for the extractive separation of benzene and cyclohexane.

In **Chapter 4**, a CAILD method based on the UNIFAC-IL model and GC-based physical prediction models is proposed for biogas upgrading. [MMPY][$Tf_2$N] and [MMPY][eFAP] are designed to be the best IL candidates by the generate-and-test method from the design space of 880 ILs. These two ILs both have a very high $CO_2$ solubility (0.37 and 0.44, respectively) and low $CH_4$ selectivity (0.01 and 0.02, respectively), which are promising alternative solvents for biogas upgrading. Moreover, all physical property constricts are met, indicating that the designed ILs possess good physical characteristics. By using the designed ILs, a process simulation for biogas upgrading is built using Aspen Plus and the corresponding parameters for the build-in equations are fitted by Matlab. To ensure the loss of $CH_4$ < 1% and minimize energy consumption at the same time, the pressure of the flashers is also investigated. The optimal pressure of the flashers for [MMPY][$Tf_2$N] and [MMPY][eFAP] are 2.1/1.9

bar and 2.0/1.7 bar, respectively. Compared to the water-scrubbing process, the advantages of the IL-based process are less solvent usage and energy consumption.

In **Chapter 5**, a practical CAILD method for the screening of suitable ILs as extraction solvents is presented and exemplified by the extractive desulfurization process. A database includes 47424 experimental $\gamma^{\infty}$ datapoints is built and used to evaluate the extractive performance of ILs towards the given extraction problem. To avoid the deviation brought by the predictive models for the physical properties, the experimental data are used when applicable. Based on this concept, the melting point, viscosity, and toxicity of the ILs are evaluated, and ILs with good extractive performance and favorable physical properties are selected. After that, the LLE experiments are performed using the selected ILs and the corresponding parameters for the NRTL model are regressed. Finally, the continuous extraction process is simulated in Aspen Plus, and the process using ILs is compared with the process using conventional solvents. The proposed method has been successfully illustrated by the extractive desulfurization problem, where [EMIM][$MESO_3$] ($S^{max} = 420.87$ and $\beta^{max} = 1.27$ for thiophene/heptane system) and [EIM][$NO_3$] ($S^{max} = 281.90$ and $\beta^{max} = 0.82$ for thiophene/heptane system) are selected as the optimal IL solvents. The processes using these ILs have significantly lower solvent consumption and heat duty compared to that of the benchmark process using sulfolane.

It is worth mentioning that all the presented CAILD methods in this thesis can be easily modified by updating the thermophysical prediction models or extended to other separation tasks by adjusting the objective function and constraints. In the future, the CAILD method could be combined with process design, which means the optimal IL structure and the corresponding optimal process configuration using the designed IL are simultaneously identified. Besides, the detailed techno-economic evaluation for the IL-involved process should also be investigated.