

Computer-aided solvent selection and design for efficient chemical processes

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The chemical industry makes extensive use of solvents, especially for chemical reactions and separations. When considering the large number of existing solvents and the necessity for finding new and alternative ones, systematic methods for the optimal selection and molecular design of solvents become significant for efficient and sustainable chemical manufacturing. During the past decade, a substantial number of contributions have been made in this area. This article summarizes property models for predicting solvent effects and introduces theoretical methods for solvent selection and design. Recent developments in computer-aided solvent selection/design for four selected application areas including reaction rate acceleration, carbon capture, extractive desulfurization, and homogeneous catalyst recovery are briefly reviewed. To conclude, several remaining challenges and possible future directions are discussed.

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Introduction

Nowadays millions of tons of solvents are used in industrial processes annually and the demand is increasing. Chipperfield [1] summarized four major applications of solvents within the chemical process industries as reactants, reaction media, separation agents, and transportation agents. As reaction media, solvents help by increasing the reaction rate and/or improving the equilibrium conversion. Solvents are also used as separation agents in various processes, such as gas absorption, liquid-liquid extraction, and extractive

distillation, where their use increases the separation factor (e.g. relative volatility). Zhou [2**] illustrated and rationalized the significant effects of solvents on reaction and separation processes from the perspectives of molecular interactions and fluid phase thermodynamics. It was demonstrated that solvent effects are closely related to certain solvent properties. Thus, our knowledge of these properties and our ability to predict them play an important role in solvent selection and design strategies.

Because of the significant effect of solvents on chemical processes, careful solvent selection is often essential for reducing process costs. In addition to this economical driving force, stricter safety, environmental, and health regulations are bolstering the transition towards greener solvents. Considering the vast number of possible solvents, the trial-and-error approach to solvent selection would be very time-consuming and costly. Moreover, the limitations in a user's experience and knowledge as well as bias may also lead to suboptimal performance of the identified solvents. With constantly improving theoretical and modeling methods, coupled with the exponential growth of computing power, it is now possible to incorporate computational methods in guiding the selection and design of solvents in more applications.

This article begins with a summary of the property models for predicting solvent effects and then introduces theoretical methods for solvent selection and design. Finally, recent works on computer-aided solvent screening and design for four selected application areas are briefly reviewed.

Solvent property modeling

It was demonstrated that solvent effects are closely related to a certain solvent property or to a set thereof [2**]. Therefore, the key to selecting or designing solvents is to find reliable property prediction models. The following section briefly discusses the methods for predicting solvent physical and thermodynamic properties.

Physical property prediction

Solvent physical properties are usually predicted using quantitative structure-property relationship (QSPR) models where the property of interest is correlated with certain molecular (usually structure-related) descriptors [3]. Typically, linear correlations are used in QSPR modeling, but when complex, nonlinear relationships exist

between the input descriptors and output property, more advanced correlation methods, such as artificial neural networks (ANN) can be used [4]. Currently, linear group contribution (GC) models are the most important QSPR models for predicting solvent physical properties [5^{*}]. In these models, the structural descriptors are the number of functional groups that comprise the molecule. The model parameters, that is, contribution of each group to the property, are regressed from experimental property data for a set of known solvents. It is worth noting that despite the popularity and effectiveness of first-order GC models, their accuracy is restricted to simple molecules due to their neglect of the group's connectivity. To predict properties for large complex molecules, more sophisticated GC models, for example, higher-order GC and ANN-GC, are recommended.

Thermodynamic property prediction

Thermodynamic models used with solvents can be classified broadly into two categories: activity coefficient models and equations of state (EoS) [6^{*}].

Prediction of activity coefficients is fundamental in evaluating solvent performance in many separation processes, such as liquid-liquid extraction and crystallization. UNIFAC [7] is a GC variant of the UNIQUAC activity coefficient model. Because of its GC basis, UNIFAC has been extensively used for solvent molecular design [8–10]. Unlike conventional models that require the use of experimental data to fit either molecular-specific or group-specific parameters, COSMO-RS [11] (commercial) and COSMO-SAC [12] (free of charge) allow for the prediction of activity coefficients based only on the σ -profiles (screening charge density distributions) of molecules. Taking into account the existing σ -profile databases, large-scale solvent screening can be performed efficiently using COSMO-RS or COSMO-SAC predictions [13,14]. Notably, a few GC methods have been developed recently for predicting solvent σ -profiles, making it possible to use COSMO-type models to perform solvent molecular design [15–17]. Because of the use of experimentally regressed group interaction parameters, UNIFAC is usually quantitatively more accurate than COSMO-type models. However, COSMO-RS and COSMO-SAC can provide qualitatively satisfying predictions on solvent performance without the need for molecular and group-specific parameters.

When selecting solvents for applications involving high-pressure vapor-liquid equilibrium (such as gas absorption and extractive distillation), an EoS is usually employed. Among different EoS models, cubic EoS are mathematically simple and show satisfying predictions of thermodynamic properties for gas and oil mixtures at a wide range of pressures [18]. These models usually require the input of pure-component critical properties. In cases where there is a lack of data or one wants to apply such models in a purely predictive way, these parameters

can be estimated by GC models [5^{*}]. With the pure-component parameters, mixture-dependent parameters can be calculated using mixing rules. The most common and simple one is the classical van der Waals one fluid (vdW1f) mixing rule [19]. An EoS using this mixing rule cannot appropriately represent highly polar species. This drawback has been solved by another type of mixing rule that incorporates an activity coefficient model into the calculation of the mixture parameters. An EoS employing such a mixing rule is called an EoS/ G^E model [20]. One of the most popular predictive EoS/ G^E models is PSRK where the SRK EoS is combined with the UNIFAC activity coefficient model. Compared to the traditional cubic EoS, EoS models based on statistical thermodynamics are more complex and can more accurately estimate liquid compressibility and the related thermodynamic properties. The most successful examples of such theory-based models are the SAFT-type models, such as PC-SAFT [21]. The model parameters can be regressed from experimental data or determined from GC methods. In fact, several GC models [22] have been developed to estimate the SAFT parameters, allowing it to be used in solvent design. It is worth noting that compared to cubic EoS, the SAFT models usually have a limited capability of simultaneously modeling the sub-critical and critical states [23]. This should be taken into account when selecting models for particular systems.

As discussed above, each model has its own strengths and weaknesses. How to address model limitations and combine the advantages of different models deserves extensive study in future works. For activity coefficient models, experimental data can be used to calibrate the COSMO-RS predictions. One can then perform large-scale solvent screening based on the calibrated model. Additionally, calibrated predictions can be used as pseudo-experimental data to regress UNIFAC group interaction parameters [24], which consequently expands the solvent design space. For EoS, Polishuk [23] built a hybrid model by adding a cubic EoS's cohesive term to the SAFT residual Helmholtz free energy (A^{res}) expression. It has been demonstrated that the resulting hybrid model preserves the advantages of both the cubic EoS and SAFT approaches. This hybrid modeling idea opens a new way to upgrade the EoS, potentially leading to more accurate predictions on solvent thermodynamic properties.

Solvent selection and design methods

Methods for solvent selection can be classified into two categories: database screening and molecular design. When performing solvent screening, a given set of solvent candidates is pre-specified and solvent molecules are usually treated as complete structures. Numerous works using COSMO-RS as the predictive thermodynamic model for large-scale solvent screening can be found in the literature [13,14,25]. Unlike in solvent screening,

whose aim is to identify the best solvent from a known set of candidates, molecular design attempts to find promising solvent molecules from the optimal combination of molecular fragments, which in most cases are functional groups. This strategy can lead to unconventional but outstanding solvent structures.

Computer-aided molecular design (CAMD), first introduced by Gani and Brignole [8], is a general term describing the procedure of rational design of molecules that possess pre-specified, desirable properties. A standard CAMD procedure consists of two steps. The first is to establish certain property models that can reliably predict molecular properties from molecular structures. The second step is to solve the reverse problem, that is, to determine the optimal molecular structure having a set of desirable properties by either generate-and-test or mathematical optimization techniques. Unlike the generate-and-test method that enumerates all possible molecules and tests them one by one against the target property [8], the mathematical optimization method finds the molecule with optimal properties by formulating and solving an optimization problem without testing all the candidates in the design space [26]. Austin *et al.* [27^{••}] provides an overview on the CAMD methodology, software/tools, and solution techniques. Since its emergence, CAMD has been widely used for designing solvents for various applications [28].

It is worth noting that in addition to solvent design, the process, in which the solvent is used also needs to be optimally designed. Two solution methods, decomposed and integrated design strategies, can be employed for combined solvent and process design. The decomposed design method [10] solves solvent and process design problems sequentially. In contrast, an integrated design strategy [29[•],30–32] attempts to simultaneously identify the best solvent and optimal process conditions. This is usually achieved by formulating and solving mixed-integer nonlinear programming (MINLP) problems.

Generate-and-test methods consider every possible structure, and it is inefficient for problems with large design spaces. Optimization methods have a distinct advantage for these kinds of problems. However, most of the solvent (and process) design problems are inherently nonconvex MINLP problems that are not easy to solve to global optimum with the current local solvers. For this reason, the development of global MINLP algorithms with an acceptable computational cost is important. In addition to pure solvents, solvent blends are also widely used in industry. The advantage of using solvent mixtures is that their properties can be well tuned by changing the composition. The inclusion of additional constraints relevant to the mixture properties makes the problem much more challenging. For tackling these problems, decomposition-based solution strategies can be employed.

Applications

In the following sections, representative works on solvent screening and design in four chosen application areas are briefly discussed. These include reaction rate acceleration, carbon capture, extractive desulfurization, and homogeneous catalyst recovery. These topics are selected due to the following considerations: Firstly, the area should already have been substantially studied, secondly, it is preferable to cover different types of solvent applications (reaction, separation, environment, etc.), thirdly, both solvent screening and molecular design, as well as organic and ionic liquid solvents, should be discussed, and lastly, we have tried to focus on solvent applications within the authors' area of competence.

Solvent design for reaction rate acceleration

The selection of solvents, in which to carry out liquid-phase organic reactions often has a large impact on reaction rate and selectivity and is thus a key decision in process design. However, in contrast to the extensive work performed in solvent design for separations, only a handful of attempts have been made in the optimal design of solvents for chemical reactions.

Quantum chemical (e.g. DFT) calculations can be used to quantify the reaction rate in different solvents. However, this procedure is usually computationally expensive. Alternatively, one can build empirical QSPR models to predict solvent kinetic effects. Folić *et al.* [33] proposed such a method for the optimal design of solvents to promote chemical reactions. They built a solvent-affected kinetic model by correlating experimental rate constants measured in a few known solvents with their corresponding solvent solvatochromic parameters. A CAMD problem was then formulated using this model and solved to identify the optimal solvent that provides a maximum rate constant. The method has been successfully applied to an S_N1 reaction. Sioungkrou *et al.* [34] extended the method to the optimal design of CO_2 -expanded solvents for a Diels-Alder (DA) reaction. The best solvent was selected from three candidates: acetonitrile, methanol and acetone and the solvent composition in the gas-expanded liquid was optimized using process economics (instead of reaction rate) as the objective function. In theory, DFT calculations can be used to predict rate constants when experimental kinetic data are unavailable. In accordance with this idea, Struebing *et al.* [35] developed a framework combining DFT computations and the CAMD method proposed in [33] to design solvents that maximize reaction rates. The reaction rate constants from a diverse set of six or seven solvents are predicted with DFT calculations and then used to parameterize the solvatochromic equation. This fitted model is later used to find optimal solvents via the CAMD strategy. Although in principle no experimental data are required, the authors claimed that the method is flexible enough to include experimental rate constants to

complement the DFT predictions as long as they are available and reliable.

Unlike previous works that employ empirical solvatochromic parameters, Zhou *et al.* [36] proposed a novel solvent screening method using theoretical descriptors to correlate the effects of solvents on reaction rate and selectivity. Based on extensive model predictions with 136 common solvents, a few promising candidates showing the highest reaction rates or selectivities were identified. The method has been successfully applied to three different organic reactions. Zhou *et al.* [29^{*}] introduced new solvent theoretical descriptors ($S_1 - S_6$, see Figure 1) based on COSMO-RS σ -profile areas. They used these descriptors to correlate solvent effects on the kinetics as embedded in the rate constant. On the basis of the parameterized kinetic model and a GC model developed to estimate the descriptors, optimal solvents with the highest predicted reaction rate constants were identified from the formulation and solution of a CAMD problem. This method has been demonstrated on a simple DA reaction, and Zhou *et al.* [37] then extended it to a competitive DA reaction with the objective of maximizing the production of the desired product relative to that of the byproduct. Liu *et al.* [17] proposed another rate constant prediction model using infinite dilution activity coefficients, hydrogen-bond strengths, and surface tension as the solvent descriptors. The established model was used to find the solvent showing the highest rate constant. Austin *et al.* [38] proposed a method to design optimal solvent

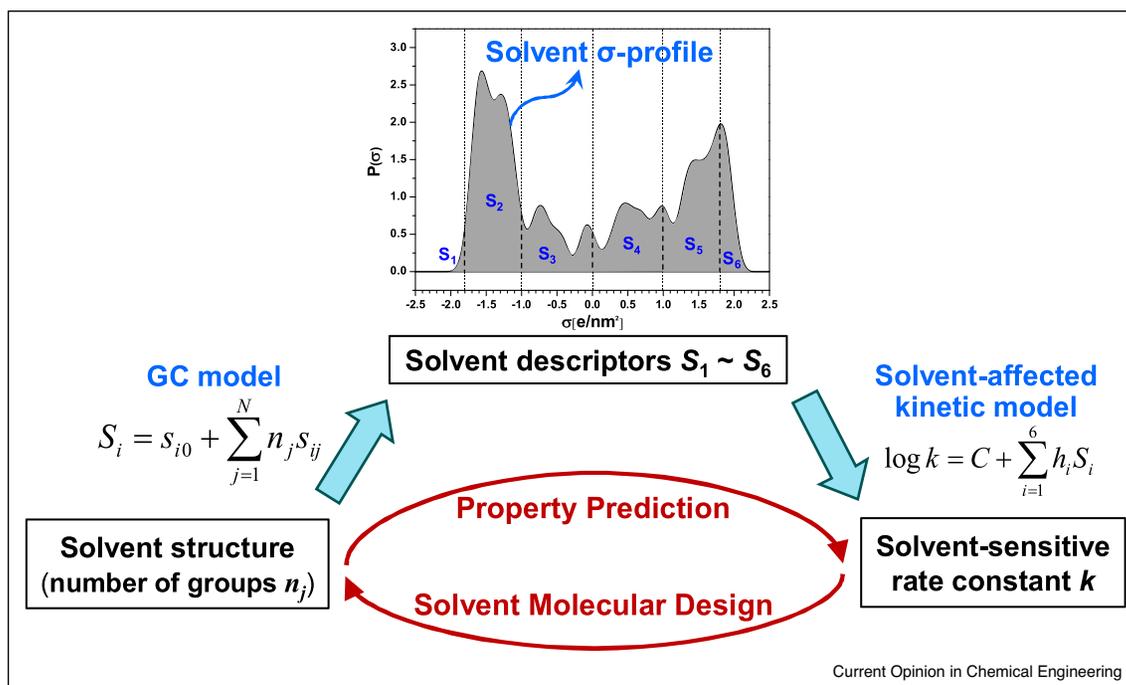
mixtures through the optimization of pure-component molecular structures and mixture compositions using COSMO-RS for property predictions. This solvent design method has been successfully applied to a few different applications including the maximization of the reaction rate of a Menshutkin reaction.

The solvent descriptors introduced in Zhou *et al.* [29^{*},37] have been proven to be good parameters for quantifying solvent effects on reaction kinetics. Because of their molecule-specific characteristics, these descriptors, in theory, can be used to correlate many other solvent properties, effects, and behaviors. This makes it possible to expand the solvent design method to other applications. Despite many achievements, challenges and limitations still exist. First, the accuracy of DFT calculations in predicting liquid-phase reaction rates needs to be improved. Second, the miscibility of the reactants with different solvents should be carefully checked in order to make sure that no phase splitting occurs when adding the solvent.

Solvent selection for carbon capture

A substantial number of works on the optimal selection and design of solvents for carbon capture have been reported. Stavrou *et al.* [39] proposed a two-stage solvent and process design method to identify promising physical solvents for pre-combustion CO₂ capture. The solvent molecule is represented as a set of PC-SAFT parameters that are simultaneously optimized along with the operating conditions of the process. Afterwards, an existing

Figure 1



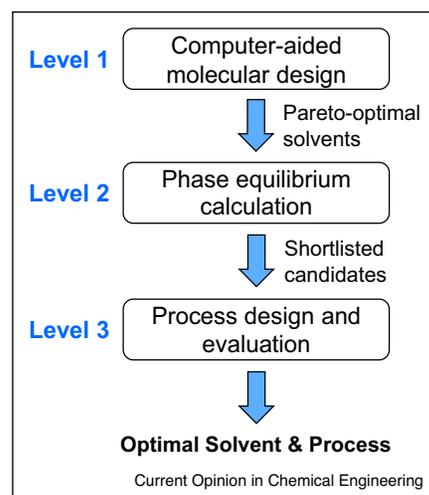
Structural framework of the reaction solvent design method proposed in Refs. [29^{*},37].

solvent is identified that most closely matches the optimal molecular parameters. Instead of relying on database mapping, Lampe *et al.* [40] employed a GC method for estimating PC-SAFT parameters to identify the optimal solvent. Burger *et al.* [32] developed another multi-level approach to tackle complex solvent and process design problems. First, the design problem based on simplified process models is solved via multi-objective optimization to generate a set of Pareto-optimal solutions. These solutions are then used as initial estimates for solving a second MINLP-based integrated solvent and process design problem where rigorous process models are applied. The method has been successfully demonstrated on a CO₂/CH₄ separation process.

Ionic liquids (ILs) are molten salts at or near room temperature and are widely used as separation solvents. Farahipour *et al.* [25] proposed a fast IL screening method using COSMO-RS to predict the activity coefficient of CO₂ in ILs and GC models to estimate the viscosity and melting point of the ILs. Hundreds of possible cation and anion combinations were evaluated which resulted in ten promising ILs for CO₂ physical absorption. Based on extensive COSMO-RS predictions, Zhao *et al.* [14] established a large database of Henry's constants of CO₂ and CH₄ in more than 10 000 ILs at 313.15K based on which optimal ILs were found for CO₂/CH₄ separation. Chong *et al.* [41] employed the CAMD method to design IL solvents for carbon capture. The UNIFAC model was used to predict CO₂ solubility in ILs and GC methods were applied to estimate the physical properties of ILs. Realizing the strong interaction between solvent selection and process operation, Chong *et al.* [42] performed integrated IL and process design for carbon capture where the best IL structure and optimal process conditions were simultaneously identified. Valencia-Marquez *et al.* [31] proposed a multi-objective optimization based method for integrated IL and process design for post-combustion CO₂ capture to handle conflicting design objectives related to process economics and environmental impacts.

Because of their strong affinities for the CO₂ molecule, chemical solvents show high potential for carbon capture, especially for the selective separation of low-concentration CO₂. Papadokostantakis *et al.* [43**] proposed a multi-scale design framework to search for chemical solvents used in CO₂ capture. As depicted in Figure 2, at the molecular level, multi-objective CAMD problems are solved to generate a set of Pareto-optimal solvents considering performance criteria that reflect solvent thermodynamic, reactivity, and sustainability properties. Later, the obtained solvents are introduced to the phase level where the chemical and phase equilibria of the solvent-water-CO₂ mixture are accurately predicted by the SAFT models, based on which solvent candidates are further short-listed. Finally, for each of the remaining solvents, the absorption-desorption process

Figure 2



Multi-scale framework for carbon capture solvent design [43**].

economics and sustainability are evaluated. On the basis of the results, the optimal solvent and process are finally identified. Limleamthong *et al.* [44] screened 125 amine-based solvents for CO₂ capture considering 10 different solvent properties relevant to technical, health, safety, and environmental aspects. The CO₂ solubility was estimated from Hansen solubility parameters. Other properties, such as viscosity and toxicity, were estimated from various empirical correlations. Zarogiannis *et al.* [45] proposed an enumeration-based approach for the screening of binary amine mixtures for CO₂ capture. Important properties were predicted by GC models, activity coefficient models, and EoS.

There has been much effort applied to the optimal design of solvents for carbon capture through physical or chemical absorption. The hybrid physical-chemical absorption combining advantages of both absorptions and hybrid separation processes combining absorption with other separation technologies (such as adsorption and membrane) have attracted much attention. Taking into account these hybrid schemes when selecting carbon capture solvents can potentially help in finding more cost-effective solutions, and thus deserves further investigation.

Ionic liquid screening and design for extractive desulfurization

Extractive desulfurization is a very important process for ultra-clean fuel production in the petroleum industry where ILs as extraction solvents have been extensively studied [46]. In this section, some important IL screening and design works are briefly introduced focusing exclusively on the extractive desulfurization process.

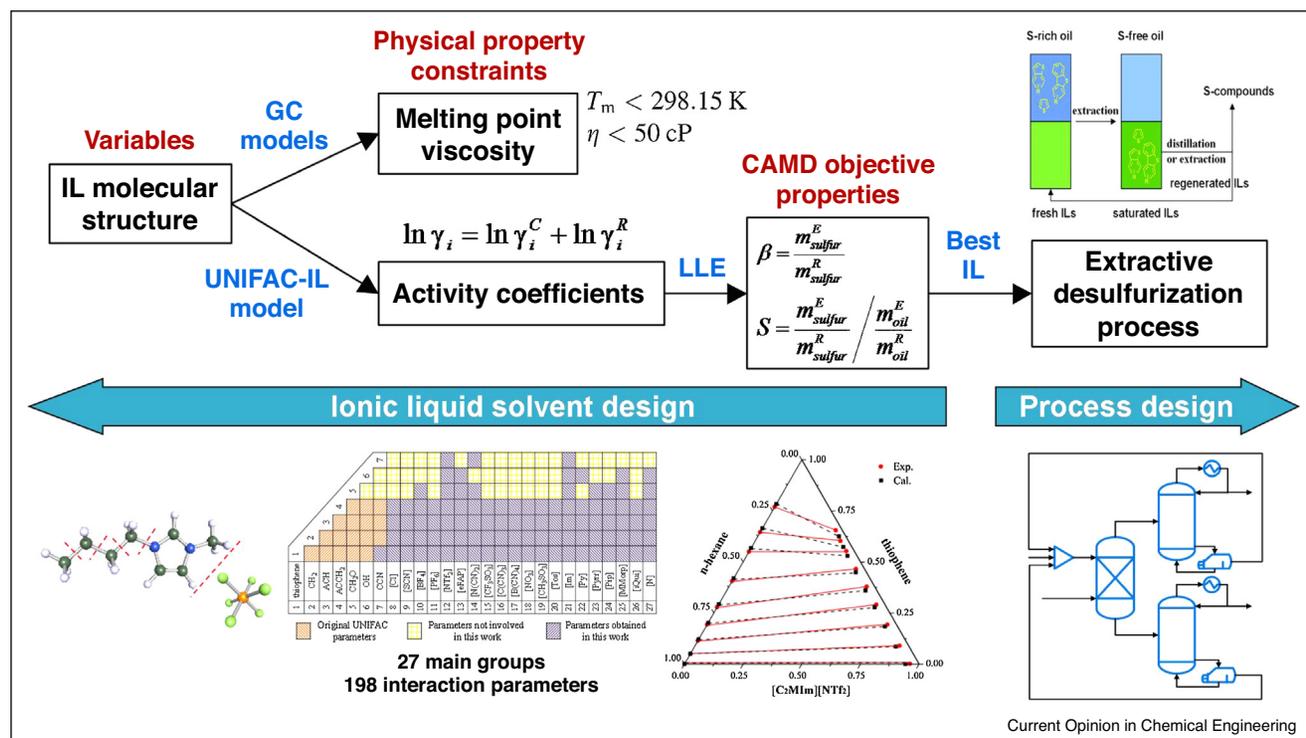
The early IL screening works on extractive desulfurization (such as Kumar and Banerjee [47]) primarily employ COSMO-based models to estimate the extraction capacity and selectivity of ILs based on infinite dilution activity coefficients (γ^∞). However, one should note that the goal of extractive desulfurization is to remove the residual traces of aromatic sulfur compounds from fuel oils. Most ILs contain nitrogen and/or sulfur and for this reason, Song *et al.* [13] suggest that IL-in- raffinate solubility should be considered along with the extraction capacity and selectivity when screening ILs for such processes. By evaluating the structural effect of cations and anions on these three thermodynamic criteria with COSMO-RS, a very promising IL solvent was found. The practicality of the solvent in extractive desulfurization was further validated by ternary liquid-liquid equilibria (LLE) and multistage extraction experiments.

Moving beyond using merely thermodynamic property estimation in IL screening, a multilevel IL screening approach was proposed to evaluate the extraction performance of ILs from multiple aspects. Song *et al.* [48^{*}] combined phase equilibrium calculations, physical property estimations, and process simulations in order to screen IL solvents for extractive desulfurization. At the first stage, the LLEs for systems composed of a model fuel oil and different ILs were calculated using COSMO-RS. It is worth mentioning that the mass-based

distribution coefficient, selectivity, and IL-in- raffinate concentration derived from LLE were employed as the thermodynamic criteria. Compared to the γ^∞ -based thermodynamic criteria, the LLE-based ones better address the effects of IL molecular weight and mixture composition on the solvent performance. This leads to the identification of more practical solvents than previously. At the second stage, several physical properties of ILs, such as melting point and viscosity, were estimated using GC methods to ensure the screened ILs are liquid and show relatively high mass transfer rate at the extraction condition. At the third stage, the process performances of the top IL candidates were analyzed using Aspen Plus to finally identify the optimal solvent. Recently, Song *et al.* [49] further extended this multilevel method to search double salt ILs (IL mixtures) for extractive desulfurization, where the γ^∞ -based and LLE-based thermodynamic properties of IL mixtures are considered instead. Compared with the screening of traditional ILs, IL mixture design provides a much larger solvent space and an easier way to tune solvent properties.

In addition to IL screening, CAMD methods have also been used to design IL solvents for extractive desulfurization. Song *et al.* [50^{*}] performed an optimal IL design study on the extractive desulfurization process following the framework depicted in Figure 3. In this work, the

Figure 3



Schematic diagram for CAMD of IL solvents for extractive desulfurization.

UNIFAC model was first extended to cover 20 IL main groups and seven conventional main groups (including thiophene) with the group interaction parameters regressed from experimental data. Then, using the resulting UNIFAC-IL model and the available GC models for predicting the physical properties of ILs, a CAMD problem for IL design was formulated. This problem was solved to optimize the LLE performance of ILs while considering constraints on the IL structure, thermodynamics, and physical properties. The top candidates identified from the CAMD optimization were further evaluated and compared to the benchmark organic solvent sulfolane by simulating the continuous extractive desulfurization process using Aspen Plus. Compared to sulfolane, the best IL solvent designed shows a negligible solvent loss and potentially leads to a more than 80% reduction in the required heat utility of the process.

Despite the progress made, the previous studies have only covered the tip of the iceberg when considering the large number of potential ILs. Important IL properties such as cost, toxicity, and biodegradability have not been considered due to the lack of reliable prediction models. Therefore, continuously developing reliable models for a wide range of IL properties is required in order to expand the current IL screening and design methods to other application areas. Besides, one should note that a certain level of uncertainty is usually associated with experimental data. A robust framework incorporating these uncertainties into the model development and IL design procedure is essential to ensure highly reliable results.

Thermomorphic solvent selection for homogeneous catalyst recovery

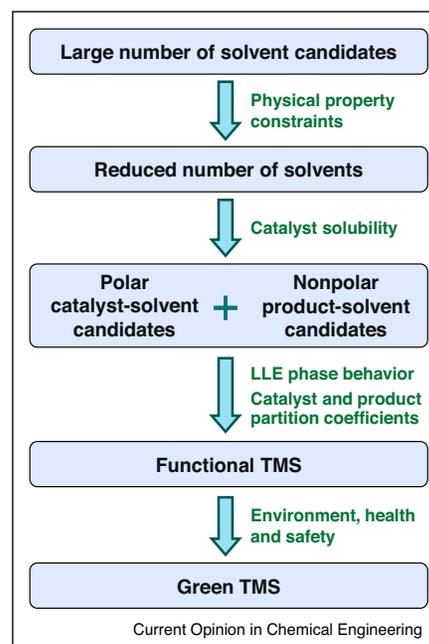
Another area where solvents play an important role is in facilitating reactions using homogeneous transition metal catalysts (HTMC). The economic feasibility of such reactions usually depends upon minimizing the amount of catalyst leached or otherwise lost during the process due to the expense of the metal and ligands comprising the catalyst complex [51]. There are many solvent-based strategies for recovering these expensive catalysts based on switchable solvent systems. Included among these are thermomorphic solvent systems (TMS) that use a simple change in temperature to induce phase switching. At reaction conditions, the temperature is high enough to ensure that a single, homogeneous phase exists. Afterwards, the product mixture is cooled and a biphasic mixture develops. The polar phase containing the catalyst is recycled back to the reactor and the non-polar phase containing the product is further processed downstream [51]. Normally, a TMS comprises three solvents with different polarities, one polar, one non-polar, and one with a polarity somewhere in between. The last solvent is called the mediator and is used to better control the miscibility behavior of the mixture. TMS may sometimes be composed of only a polar catalyst solvent and a

non-polar product solvent without an additional mediator solvent, whose role is instead performed by one or more of the reactants. A recent review by Bianga *et al.* [52] presents a comprehensive list of recent TMS used in reducing catalyst leaching in HTMC supported reactions.

As is common, choice of the solvent may exhibit a strong influence on process performance and selecting the right TMS component solvents for a specific application may not be trivial. In the literature, the primary design methodology uses heuristics and expert knowledge to determine promising TMS solvents. Behr *et al.* [53] proposed a design strategy for TMS composed of three solvents. Initially, the polar and non-polar solvents are fixed and the mediator is chosen such that the TMS phase switching is achieved in the desired temperature range. For selecting the mediator, five criteria are introduced: polarity, being liquid at ambient conditions, miscibility with the polar and nonpolar solvents, and being stable during reaction. Functional mediators for novel TMS were identified using this approach.

Another strategy, this time for two-solvent TMS design, is a database-driven screening approach using thermodynamic property predictions made by COSMO-RS to identify solvents [54*,55]. A depiction of this method is presented in Figure 4. McBride *et al.* [54*] applied this approach to the hydroformylation of 1-dodecene using an Rh-BiPhePhos catalyst complex. In a hierarchical procedure, the solvent search space is first reduced according to certain physical property constraints, such as the boiling

Figure 4



The methodology for green TMS solvent screening [54*,55].

point and molecular weight limitations. Afterwards, the catalyst solubility in each solvent is calculated with COSMO-RS. In accordance with the solubility ranking, polar and nonpolar solvent pairs that can potentially form TMS are screened. The LLE behavior as well as product and catalyst partition coefficients are predicted to identify which TMS (solvent pairs) are functional, and the most promising candidates are subsequently investigated experimentally. Surprisingly, the TMS comprising dimethylformamide and n-decane, which has already been used in previous experimental studies, was found to be one of the most suitable TMS for the hydroformylation application. Although no improved TMS was found, this work was successful in bridging a gap between expert knowledge and experimental findings with computational methods. Taking into account environment, health, and safety (EHS) criteria, McBride *et al.* [55] refined the TMS solvent screening method to identify functional TMS composed of green solvents for a similar hydroformylation reaction (see Figure 4).

Although several methods for determining TMS constituent solvents have been developed, one remaining and substantial difficulty lies in predicting the solvent effects on the reaction, especially on catalyst stability and activity. This is a complex problem that demands either a deep understanding of the reaction mechanism or suitable amounts of experimental data for data-driven model development.

Conclusion

Solvent selection is a key factor in chemical process industries due to their substantial effects on process performance. In view of the overwhelming number of existing solvents and the necessity for exploring new alternative solvents, systematic methods for the optimal selection and design of solvents is essential. This article provides a brief overview on the modeling and prediction of solvent properties. Methods for solvent selection and design are introduced. Recent works on computer-aided solvent screening and design for reaction rate acceleration, carbon capture, extractive desulfurization, and homogeneous catalyst recovery are reviewed.

Despite the amount of progress made in solvent selection and design, challenges remain. Much of the previous work focuses on maximizing some measures of solvent performance. However, one should note that solvent cost, availability, and environmental impact are also important factors. The simultaneous consideration of these criteria and the solvent performance is significant for future solvent selection frameworks. Property prediction lies at the heart of solvent design and in some cases where simple GC models are not able to provide accurate predictions on solvent physical properties, more powerful QSPR models can be used. These include those based on higher-dimensional structural descriptors (e.g. topological

index) or those using advanced correlation methods, such as more complex methods within the machine learning discipline. The efficient incorporation of GC models, complex QSPR models, and predictive thermodynamic models into a solvent design framework is important. Because of the possible deviations of the employed property models, the performance of the computationally screened or designed solvents should naturally be verified by experiment.

Conflict of interest statement

Nothing declared.

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