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Multiscale Modeling of Liquid-Liquid Phase Transfer Catalysis for the Simultaneous Extraction and Conversion of Hydrogen Sulfide to Value-Added Products

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Abstract

Phase transfer catalysis (PTC) is a general methodology applicable to a wide variety of reactions in which inorganic and organic anions, carbenes and other active species react with organic compounds. The basic principle of PTC is that the reactions take place in heterogeneous two-phase systems (organic-aqueous) with negligible mutual solubility of the phases. The organic phase consists of organic reactants (neat or in organic solvents), whereas the aqueous phase contains inorganic salts/bases. The catalyst, located in the aqueous phase, acts as a source of lipophilic cations and continuously introduces the reacting anionic species in the form of lipophilic ion pairs into the organic phase. This type of two-phase system offers numerous advantages, such as high yields and purity of the products, operational simplicity, mild reaction conditions, suitability for large-scale synthesis, and an environmentally benign nature of the reaction system.[i,ii,iii]

However, the downside of PTC is the need to quantify exacting reaction conditions and parameters that are difficult to uncover and, in some cases, are counterintuitive.[ii] In a 1998 comprehensive review of the field from an engineering perspective,[iv] the authors lamented the lack of published theoretical process modeling for scale-up and concluded that this has hurt the commercialization potential of PTC. Although the next two decades have seen some progress in terms of mathematical modeling of PTC systems,[v,vi,vii] availability of accurate thermodynamic parameters still proves a major limitation as the chemical domain in the group contribution methods, such as UNIFAC, is inherently limited to the portion of the chemical design space for which every binary interaction parameter is available.

In this respect, COSMO-based models, such as COSMO-RS,[viii,ix] are valuable alternatives for describing liquid-phase thermodynamics with the major advantage of not requiring any binary interaction parameters to calculate chemical potentials and, consequently, free energies of solvation. Furthermore, COSMO-RS allows for easy integration of quantum chemical calculations into a process modeling framework, greatly expanding the envelope of chemical species that can be modeled at a high level of accuracy.

The primary objective of this work is to develop a rigorous multiscale mathematical model to demonstrate the application of PTC to hydrogen sulfide recovery and conversion from an aqueous alkanolamine solution to value-added organic products to improve process economics and sustainability. Desulfurization of sour natural gas has been an increasing concern for the energy industry due to the high economic and environmental cost of the existing technologies. Application of PTC to this problem can effectively overcome these issues by providing a waste-to-value pathway toward resource recovery and circular economy.

With Python as the high-level interface, the solution algorithm uses varying tools for different scales of time and space to model and predict the behavior of the system: Turbomole at quantum mechanical/continuum solvation level, COSMOtherm at solvent/mixture level, and Pyomo at process/systems level. A dynamic-programming approach is employed to solve the resulting nonlinear optimization problem using the IPOPT solver.

By combining these tools in a novel integrated scheme, we can identify the extent of possible reaction pathways leading to the design of intensified unit operations in an optimization-based integrated product-process design framework. The proposed methodology can be furthered used as a basic platform to simulate similar systems. Herein, the multiscale model described above is applied to the identification of catalyst/product(s), optimization of the organic solvent and design of the intensification process, turning the hazardous by-product of natural gas processing into a value-added product.

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