Intensification Mechanism and Processes

CAS/MPG Partner Group on Intensified Processes

Shanghai-Magdeburg, 2010.1.1–2014.12.31

Prof. Dr.-Ing. Kai Sundmacher (right) visits the Partner Group headed by Prof. QI Zhiwen (left) and receives his Guest-professorship from the East China University of Science and Technology in Shanghai.

After six years of fruitful research with Prof. Dr.-Ing. Kai Sundmacher at the Max Planck Institute for Dynamics of Complex Technical Systems (MPI Magdeburg), Dr. QI Zhiwen joined the State Key Laboratory of Chemical Engineering at the East China University of Science and Technology (ECUST Shanghai) in 2008. Motivated by their common research interests in the field of process intensification, the Partner Group between MPI Magdeburg and ECUST Shanghai was established in December 2009.

The Partner Group is devoted to better understanding of the process intensification mechanism and developing applicable methodology for screening innovative solvents bridging chemistry and engineering, with emphasis on reaction, separation and catalyst synthesis. In the past three years, the cooperation focused on developing a methodology based on multi-scale simulation and its application in chemical and biochemical processes.

Reported by Group Leader Dr. QI Zhiwen

Photos/Images: By courtesy of Prof.QI Zhiwen.

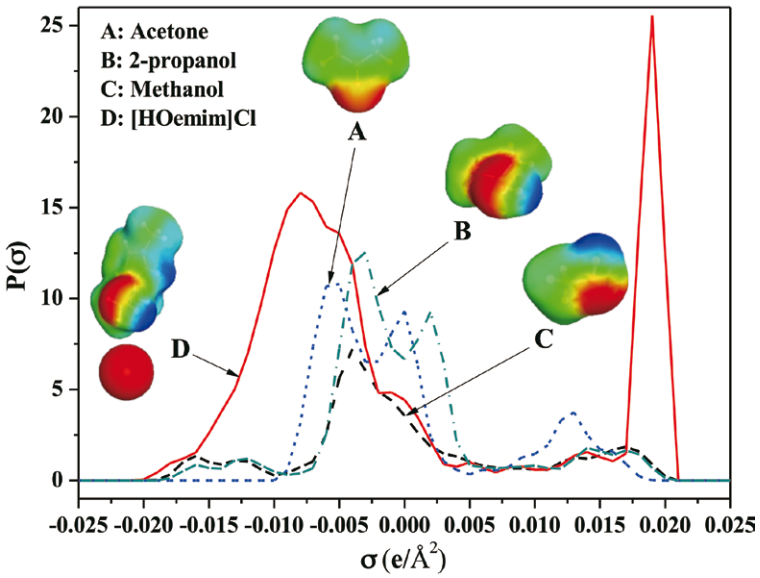

Figure 1: Shown are the σ-Profiles and COSMO-cavities of solvent molecules.

CURRENT ACTIVITIES

1. Development of methodology for solvent screening based on multi-scale simulations

One major challenge of solvent-involved processes is to understand the mechanism underlying solvent effects and to screen proper solvents for a task-specific process. The developed approach based on multi-scale simulation integrates quantum chemical calculation, thermodynamic prediction, and process simulation, and is tailored for designing and screening suitable solvents, particularly innovative solvents such as ionic liquids.

From quantum chemical calculations based on the DFT theory, geometrical parameters, and the interaction energy between candidate ionic liquids and the mixture are calculated, and types of suitable cations and anions can be suggested. Starting from this and with help of the COSMO-RS theory, thermodynamic properties of the screened ionic liquid as well as the mixture can be predicted and confirmed by experiments, and eventually the best solvent can be figured out. Finally, the process performance can be simulated and optimized with the fitted model parameters.

2. Intensification effect of solvent in reaction and separation processes

In chemical reactions and separation processes, solvent properties, *e.g.* polarity and solubility, can dramatically enhance the process efficiency. Therefore, it is essential to understand the mechanism of solvent intensification in processes and suitable solvent should be tailored for a task-specific process. For example, in selective oxidation, ionic liquid [HOemim]Cl is found to effectively intensify cyclohexanol oxidation and result in a 100% conversion of cyclohexanol with 100% selectivity to cyclohexanone, using hydrogen peroxide as an oxidant and WO_3 as catalyst. The effect of ionic liquid as solvent has been explained with the support of COSMO-RS theory (Figure 1).

For complete separation by extractive operation, *e.g.* deep desulfurization of gasoline and cyclohexane-benzene mixture, process performance can be significantly improved by designing a suitable solvent. Through molecular simulation, a promising solvent of $[C_4mim][H_2PO_4]$ (Figure 2)

SELECTED PUBLICATIONS

1. **Chen, L.; Zhou, T.; & Chen, L.F. *et al.***, (2011) *Chem. Commun.*, 47:9354–9356
2. **Zhou, T.; Wang, Z.Y.; & Chen, L.F. *et al.***, (2012) *J. Chem. Thermodyn.*, 48:145–149.
3. **Zhou, T.; Wang, Z.Y.; & Ye, Y.M. *et al.***, (2012) *Ind. Eng. Chem. Res.*, 51:5559–5564.
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5. **Chen, L.F.; Jeong, G.J.; & Schulze, M. *et al.***, (2012) *ChemCatChem*, 10:1662–1667.
6. **Chen, L.; Chen, L.F.; & Ye, Y.M. *et al.***, (2012) *Catal. Commun.*, 28(11), 143–146.
7. **Li, J.; You, C.J.; & Chen, L.F. *et al.***, (2012) *Ind. Eng. Chem. Res.*, 51:12081–12088.
8. **Tong, L.W.; Chen, L.F. & Ye, Y.M. *et al.***, (2013) *Chem. Eng. Process.*, 67:111–119.
9. **Chen, L.F.; Hu, J.C.; &Lin, F. *et al.***, (2013) *CrystEngComm*, 15:3780–3784.
10. **Tong, L.W.; Chen, L.F.; & Ye, Y.M. *et al.***, (2014) *Chem. Eng. Sci.*, 106:190–197.

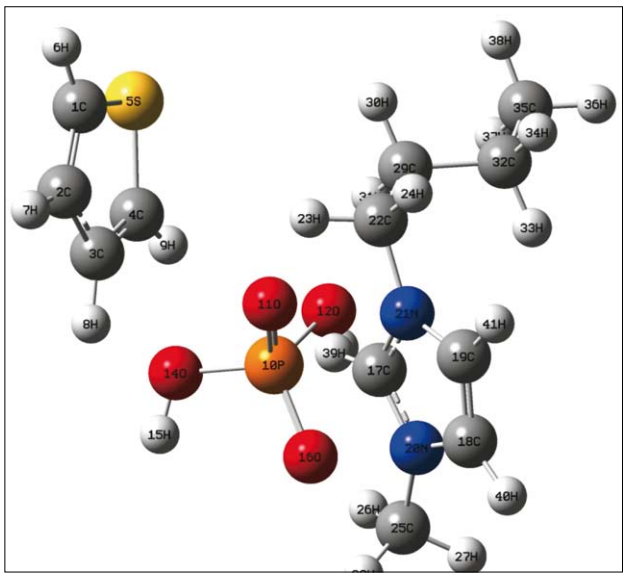

Figure 2: Optimized structure and interaction distance of $[C_4mim][H_2PO_4]$ and thiophene.

INFO

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is figured out to extract thiophene from gasoline, while its content can be kept at a very low level (< 2 ppm). Following this methodology, process validation for possible industrial application is under way. The successful application of the developed multi-scale methodology for several processes demonstrates its great applicability to solvent screening, including screening of ionic liquids for wide separation processes.

FUTURE COOPERATION

The MPI Magdeburg and the Partner Group will work further on with complementary and strong interests in innovative solvent intensified processes. The two sides will focus on two fields as stated below.

One common interest shared by the two sides is to intensify the transformation of bio-based platform chemicals, *e.g.* 5-Hydroxymethylfurfural (HMF) and succinic acid, from renewable resources to chemical products. In order to develop a green process, metal catalysts with atomical dispersion are attractive to maximize atom efficiency, and ionic liquids as suitable solvents, templates, stabilizers and promoters are expected to lead to the methodology of atomically dispersed noble metal catalysts and transformation processes of platform chemicals.

Further common activities will be the extension of the multi-scale methodology for solvent-switchable processes. The properties of solvents in operation conditions, *e.g.* temperature and pressure, will be intensively investigated, and the thermodynamic properties of the solvent-containing mixture can be analyzed and applied for coupled processes. The accuracy of simulation for the case of mixture with strongly polarized components will be especially concerned. ◂