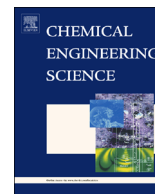




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# Model-based method for the screening of solvents for chemical reactions

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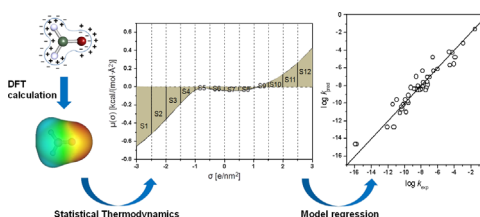
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## HIGHLIGHTS

- A new model-based methodology for the screening of chemical reaction solvents was developed.
- Solvent descriptors were determined from COSMO-RS quantum chemical computations.
- The methodology yields a good description of solvent effects on selected  $S_N1$ ,  $S_N2$ , and Diels–Alder reactions.
- Most suitable solvent candidates were identified for each studied reaction.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 16 August 2013

Received in revised form

28 October 2013

Accepted 10 November 2013

## Keywords:

Solvent selection

Chemical reactions

COSMO-RS

Molecular descriptors

Quantitative structure-property relationship

## ABSTRACT

The selection of solvents is one of the most important factors in the early stage of chemical reactor design due to significant effects of solvents on both reaction kinetics and thermodynamics. In view of a large number of potential candidates, systematic methods are strongly required for guiding the solvent selection procedure. Unlike conventional solvent selection methods, which employ empirical or experimental parameters, the present work proposes a novel solvent screening method using theoretical descriptors to quantify solvent effects. These solvent descriptors are determined from COSMO-RS quantum chemical computations and advanced statistical analysis techniques. A model is developed by correlating a limited set of experimental reaction properties (reaction rate or reaction selectivity) in various solvents with the corresponding solvent descriptors. This model yields satisfactory solvent rankings for essential target properties. Based on extensive model predictions with 136 common solvents, a few promising candidates showing the highest reaction rates or selectivities were identified and their electronic and structural properties were characterized. The reliability of the proposed method was validated with three different reactions. As the underlying COSMO theories are solely based on molecular structure information, the method is a powerful tool for fast solvent pre-screening without the need for extensive experiments.

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## 1. Introduction

Solvents are widely used as reaction media in liquid phase chemical processes. It has been proven that the variation of the type of solvent can dramatically change the reaction rate and also the equilibrium composition (Reichardt, 1988). Therefore, the

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choice of solvents has a strong impact on the development of an efficient chemical process. In the past, solvent selection was normally based on some physical constants, such as heat of vaporization, boiling point, surface tension, density, etc. As the only available solvent properties at that time, they were used to guide the solvent selection for many years. Later on, multi-parametric correlation methods were developed (Kamlet and Taft, 1976; Taft and Kamlet, 1976; Kamlet et al., 1977; Abraham et al., 1988; Palm and Palm, 1993). These methods have been widely used in the quantification of solvent effects. But they require some experimentally determined parameters. Related experiments are often time-consuming, thus they are available for a limited number of solvents and reactions only.

Considering the huge number of common solvents, one has to make use of reliable theoretical methods to guide the selection. Over the last few decades, the Computer-Aided Molecular Design (CAMD) method has been widely used for solvent screening and design (Giovannoglou et al., 2003; Karunanithi et al., 2005; Gernaey and Gani, 2010). However, it should be noted that until now CAMD studies are mainly focused on solvents for separation processes, mostly importantly for extraction (Wang and Achenie, 2002; Lei et al., 2006), extractive distillation (Chen et al., 2005), and crystallization (Karunanithi et al., 2006). There are very few systematic methods guiding the selection of solvents for chemical reactions. Stanescu and Achenie (2006) theoretically studied solvent effects on the kinetics of the Kolbe-Schmitt reaction using DFT (Density Functional Theory) calculations. In that work, solvents were screened based on the assumption that a solvent with the same solubility parameter as the product will stabilize the product and therefore improve its yield. The applicability of this method is quite limited because the solubility parameter criterion is insufficient for reactions involving polar species as reactants or transition states. Gani et al. (2005, 2008) developed a systematic method for the selection of solvents for organic reactions. With knowledge from industrial practice, physical insights, and estimated solvent properties, a set of reaction-solvent property indices were collected and converted into the corresponding scores. Desirable solvents were then specified based on the obtained scores. The method shows a strong suitability for certain reaction systems. But it requires a large amount of knowledge on both reactions and solvents to build the score table. In addition, the method cannot give

quantitative prediction on solvent effects. More recently, Folić et al. (2007, 2008) proposed an empirical model relating reaction rate constants with solvent solvatochromic parameters which were estimated from group contribution methods. By solving an optimization problem, the model yields solvent molecules for achieving maximum reaction rate constants. But this approach cannot well distinguish between isomers and many of the generated molecules are not standardly used as solvents.

Over the past decade, chemical engineers got much better access to theoretical chemistry tools and the computer power has reached a very high level. This opens the possibility to make use of theoretical descriptors for correlating solvent effects. Theoretical descriptors are easy-to-generate and do not require any experiments. In theoretical chemistry, liquids are usually treated by Continuum Solvation Models (CSMs). COSMO (Conductor-like Screening Model) is one of the most popular CSMs based on uni-molecular quantum chemical computations. Its extension towards realistic solvents, COSMO-RS, is often applied as a valuable tool for the prediction of physical and thermodynamic properties of fluid phases (Palomar et al., 2007; Peters et al., 2008; Lei et al., 2007; Burghoff et al., 2009; Deglmann et al., 2009). In COSMO theories, fundamental property functions, such as the  $\sigma$ -profile and the  $\sigma$ -potential, are derived from molecular structure information. Due to their charge-related and molecule-specific characteristics, these property functions have been successfully applied to a variety of areas, such as the interpretation of complex molecular interactions (Mohanty et al., 2010; Ortega et al., 2008; Kahlen et al., 2010), stereoisomer differentiation and separation (Lapkin et al., 2010), solvent classification (Durand et al., 2011), drug similarity prediction (Thormann et al., 2006), etc. Compared to conventional group contribution methods, COSMO-RS treats solvents with their real molecular structures. Consequently it can well distinguish between isomers.

In summary, classical solvent selection methods are mostly based on experimentally determined properties. These properties are available for a limited number of solvents only, due to time-consuming experimental measurements. Theoretical methods, such as CAMD methods, allow for the consideration of a large number of solvents. However, these methods are still limited in their ability to predict suitable solvents for chemical reactions. The present work proposes a novel model-based solvent screening

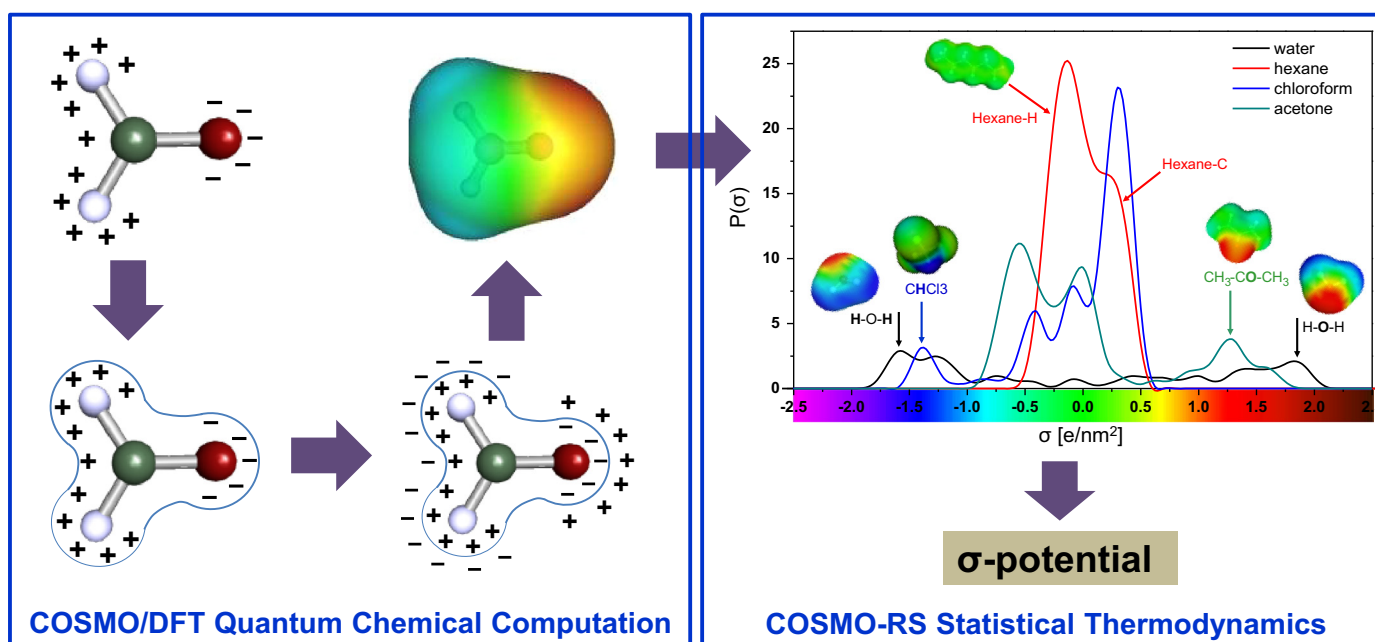


Fig. 1. Schematic diagram of COSMO and COSMO-RS methods.

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