C. R. Chimie xxx (2018) 1–16

Contents lists available at ScienceDirect

Comptes Rendus Chimie

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Computer-aided product design of alternative solvents based on phase equilibrium synergism in mixtures

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ARTICLE INFO

Article history:
Received 19 December 2017
Accepted 9 April 2018
Available online xxxx

Keywords:
Alternative solvent
Computer-aided product design
Extraction
Volatile aroma compound
Azeotropic mixture

ABSTRACT

A systematic methodology is proposed to find binary azeotropic mixtures as new alternative solvents for the extraction process of volatile aroma molecules widely used in perfume and cosmetic industries. We investigated the use of the reverse engineering approach with computer-aided product design (CAPD) instead of the traditional "trial and error" approach. First, the design problem is defined from the real functionalities of the classical solvents. The latter are translated into physicochemical properties and the corresponding boundary values for each property are defined. The reverse engineering method coupled with CAPD consists in using optimization techniques for building molecular structures that match as best as possible the complete set of target physicochemical properties, thus defining for each candidate a performance index. Property values are evaluated by using group contribution methods for each molecular structure generated by a CAPD tool or by using database values. Acknowledging the contradictory relationship between two selected physicochemical properties, that is, low boiling temperature and high flash point, which is rarely found in pure components, binary azeotropic mixtures were studied to enhance the global performance of solvent candidates. Dimethyl carbonate used as a solvent for the extraction of aroma molecules from plants exhibits between the boiling temperature and the flash point. It was selected as the key component for designing binary azeotropic mixtures. The global performance of the binary azeotropic mixtures was verified by means of calculations of the vapor–liquid and liquid–liquid equilibrium using modified universal functional activity coefficient (UNIFAC) method as a thermodynamic method.
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1. Introduction

All industries are now facing severe environmental constraints imposed by regulations concerning volatile organic compounds (VOCs) and occupational diseases (European directives 2010/75/EC, 2001/81/EC, 2004/73/EC, REACH, Clean air act, etc.). Progressively they are looking for more sustainable solutions to limit risks and hazards for health and environment. It is also an opportunity for industry to set themselves apart from the competition and to respond to the growing of consumer demands for safer and healthier products. Solvents are the most affected among all commodity chemicals by these regulations [1,2] because of their large-scale use in a significant number of industrial applications. Currently, there are two classes of solvents that are being used in industrial practice: petrochemical-based solvents and solvents from agricultural resources,

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https://doi.org/10.1016/j.crci.2018.04.005
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Please cite this article in press as: I. Rodriguez-Donis, et al., Computer-aided product design of alternative solvents based on phase equilibrium synergism in mixtures, Comptes Rendus Chimie (2018), https://doi.org/10.1016/j.crci.2018.04.005

the so-called “biobased solvents”. Although solvents from oil resources predominate in industrial applications, the chemical industry is willing to implement more sustainable solutions. It concerns especially industries devoted to produce plant-based products in food, cosmetics, fragrances, and pharmaceutical ingredients and where solvent extraction and purification techniques are at the heart of the manufacturing process that need a huge consumption of tailor-made solvents. In particular, *n*-hexane has been used for decades in extraction of aromas in food, cosmetics, fragrances, and pharmaceutical industries [3]. This solvent offers suitable performances because of its low boiling temperature and low polarity. Although many studies have demonstrated the toxic and hazardous effects [4–6], hexane is still the preferred solvent for the extraction of aromatic compounds despite its top-ranking position in the list of the hazardous solvents.

Previous studies have dealt with the *n*-hexane substitution for aroma extraction [6,7], but the screening of nonpolar and polar alternative solvents was carried out using experience-based approach. The main criteria for the solvent screening are based on the calculation of the Hansen solubility parameters (HSPs) allowing the evaluation of the affinity between the solvent and each target molecule contained in agricultural resources. Recently, Sixt et al. [8] highlighted the required coupling of the solvent screening methodology with the process design including all typical unit operations in the manufacturing of natural products. Rigorous modeling of solid–liquid extraction, purification by liquid–liquid extraction, distillation, and crystallization must be related to the physicochemical properties representing the affinity between solvent and solutes. The authors used conductor-like screening model for realistic solvents (COSMO-RS) [9] as a predictive model for computing the solubility of the target molecules in every solvent. However, the initial selection of the solvent candidates was again carried out by an experience-based approach. Because of the heterogeneous composition of the extract from bioresources, the entrainer selection based on the trial and error method is limited and may have missed good candidates. Instead, reverse engineering approaches, like computer-aided molecular design (CAMD), are fit to handle several properties simultaneously and to propose very diverse molecular structures matching the target values of these properties.

Nowadays, CAMD approach has become a standard tool for finding single molecular structures matching target physicochemical properties selected a priori by the end-user [10]. CAMD is based on a reverse engineering approach where a complete set of physicochemical properties is first established, and then the building of molecular structures is guided by the closest matching to these properties. The computer-aided product design (CAPD) tool follows the general methodology of a CAMD tool but considering the mixture as another feasible solution for which the composition of each component is also determined. The increasing application of a CAPD tool for replacing substances highly restricted by registration, evaluation, authorization and restriction of chemicals (REACH) regulations has provided some successful results mainly in designing alternative solvents for zero CFC refrigerant and biobased polymers [11]. The substitution of hazardous solvents prevails in manufacturing processes such as perfume, cosmetics, pharmaceutical, food ingredient, nutraceutical, biofuel, or fine chemical industries because solvents are widely used in huge amounts for organic synthesis, extraction, purification, and formulation processes. Recent trends in natural product chemistry have essentially focused on finding new technological solutions for reducing the use of solvents or substituting petroleum-based solvents [12–15]. We have recently developed the IBSS CAMD tool (InBioSynSolv) as a new CAPD computational tool to generate virtual molecular structures of promising solvents for a wide application spectrum in process engineering [16]. IBSS CAMD tool optimizes simultaneously the molecular structure of the component as maximizing a global performance function defined as weighted sum of the individual performance of each target property. The main advantage of IBSS CAMD over the well-known computational tool Virtual Product–Process Laboratory [17] lies on the possibility of the design of biobased solvents by fixing a chemical synthon corresponding to a fragment of an existing molecule in nature [18]. Addition and modification of free connections with external chemical groups are carried out during the optimization method of maximizing the global performance function. As a solution, the IBSS CAMD tool provides a list of best candidates including existing or new molecules. If nonadequate solution is found by designing pure components, the problem of substituting a molecule may result in proposing mixtures where synergetic nonideal thermodynamic behavior may improve properties in a nonlinear manner.

In this article, we have taken the advantages of a CAPD approach to design new alternative solvents as part of *n*-hexane substitution to extract a group of typical aroma molecules from agricultural resources that are largely used in perfumery. First, the context of the optimization problem formulation by using the IBSS CAMD tool is described. Second, a set of target physicochemical property values matching the specifications of this project is defined allowing the evaluation of the global performance function for each solvent candidate. To build molecular structures, a set of chemical fragments was selected based on the better promising green solvents reported [19] along with the incorporation of other chemical functional groups for which the fluid global performance was expected to be sensitive. Then the CAPD search was run with the help of the IBSS in-house genetic algorithm optimization technique to build new molecular structures. For each molecule, group contribution models in the IBSS property package library were used to predict the target physicochemical properties and further compute the global performance index. This led to a first list of promising candidates as pure fluids that can be further used as a niche for generating azeotropic mixtures to improve the global performance of the pure component candidates.

2. Problem formulation of a CAPD approach for the design of alternative solvents

The systematic methodology uses the reverse design approach [15,16,20] where the targets of the design

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