Chemical Engineering Science 159 (2017) 58–68

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Computer-aided ionic liquid design for separation processes based on group contribution method and COSMO-SAC model

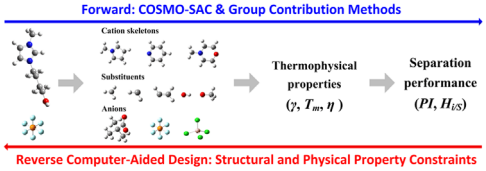
Daili Peng, Jianan Zhang, Hongye Cheng, Lifang Chen *, Zhiwen Qi *

Max Planck Partner Group at the State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

HIGHLIGHTS

- A computer-aided ionic liquid design methodology (CAILD) is developed.
- Extended GC-COSMO is established to estimate σ-profile and cavity volume of an ionic liquid.
- Contribution parameters of 61 cation groups are regressed and validated.
- The CAILD methodology is tested by examples of extraction and absorption.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 November 2015
Received in revised form
14 May 2016
Accepted 19 May 2016
Available online 25 May 2016

Keywords:
Computer-aided ionic liquid design
COSMO-SAC
Group contribution
MINLP
Separation process
CO_2 absorption

ABSTRACT

For design of ionic liquid (IL) solvents for a specific separation process, a computer-aided ionic liquid design (CAILD) method based on multi-scale simulations is presented. A new group contribution based approach GC-COSMO for ILs is established for estimating the σ-profiles and cavity volumes of cations, where ILs are structured by three parts, i.e., one anion, one cation skeleton, and substituents on cation skeleton. Prediction models, including the COSMO-SAC model for thermodynamic properties and semi-empirical models for physical properties, are integrated into a computational IL design framework. A mixed-integer nonlinear programming (MINLP) problem is then formulated to optimize the separation performance combing the constraints of structural feasibility and physical properties. The optimal IL solvents are identified using a deterministic optimization method with branch and bound algorithm. The CAILD method is successfully tested for two typical separation examples, i.e. extraction of benzene from cyclohexane and post-combustion CO_2 capture.

1. Introduction

Due to their very attractive physical properties, such as negligible vapor pressure, high thermal, chemical stability and wide liquid-phase range, ionic liquids (ILs) are widely considered as a novel solvent in separation processes (Berthod et al., 2008; Zhang et al., 2014). In addition, as a designer solvent, its physical and chemical properties can be tailored by judicious selection of cations, anions, and substituents. However, there exists a large library of ILs, which causes challenges to find proper ILs for a specific separation problem (McLeese et al., 2010). Traditional practice for IL solvent screening is guided by trial and error approaches, which are time and labor intensive, and strongly dependent on the experience and experiments. Very often, such screened ILs are not optimal as the experimental study is not realistic to reach all possible ILs.

In order to design proper ILs for a specific separation problem from theory, a reliable thermodynamic prediction model is crucial. So far, various approaches for calculating activity coefficients for IL-containing systems have been developed, e.g., classical models NRTL and UNIFAC (Alonso et al., 2007; Lei et al., 2012, 2009) and models based on statistical associating fluid theory PC-SAFT (Paduszyński and Domańska, 2012). Besides, as a quantum mechanics based predictive approach, the COSMO-based models such

* Corresponding authors.
E-mail addresses: lchen@ecust.edu.cn (L. Chen), zwqi@ecust.edu.cn (Z. Qi).

http://dx.doi.org/10.1016/j.ces.2016.05.027
0009-2509/

Nomenclature

An	group set for anion
a^+, b^+	contribution of the cation group for viscosity
a^-, b^-	contribution of the anion group for viscosity
Ca	group set of cation skeleton
d_{mn}	distance between segments m and n
D_i	diffusivity of gas i
f_i	fugacity of gas i
ΔH_{sol}	enthalpy of solvation
$H_{i/S}$	Henry's law constant in unit of bar
h_c	contribution of the cation group for surface tension
h_a	contribution of the anion group for surface tension
$K_{i/s}$	Henry's law constant in unit of $Pa \cdot m^3/mol$
LB	lower bound vector
PI	performance index of extraction
P	pressure
P_i	partial pressure
$_{pi}(\sigma_m)$	the surface area with a charge density of σ_m in cation i
$Q(i,j)$	frequency of group j in cation i
r_n	radius of segment n
Sub	substituents
Sub^*	substituents except for CH_3 and CH_2
S	selectivity of extraction
ΔS_{sol}	entropy of solvation
T_m	melting temperature
T	temperature
Δt_c	contribution of the cation group for melting point
Δt_a	contribution of the anion group for melting point
UB	upper bound vector
ν	group frequency
e	group valence
x_i	mole faction of species i in the liquid phase

Greek letters

τ	surface tension
β	distribution coefficient of extraction
γ	activity coefficient
η	viscosity
σ	surface screening charge density

Superscript

G	ionic liquid group
∞	condition of infinite dilution

Subscript

a	anion group
c	cation group
i	species i
IL	ionic liquid
k	the number of group types
S	solvent
sol	solvation

as COSMO-RS (Klamt, 1995) and COSMO-SAC (Lin and Sandler, 2002; Wang et al., 2007) have been proven to be powerful tools for calculating thermodynamic properties.

In computer-aided ionic liquid design (CAILD) for separation processes, the UNIFAC model has already been used (Karunanithi and Mehrkesh, 2013; Roughton et al., 2012). As the interaction parameters between the functional groups of ILs in the UNIFAC model are regressed from experimental data and many of them are always missing, the CAILD method based on the UNIFAC model is nowadays restricted to the limited subsets of anions and cations.

On the contrary, COSMO-SAC is a predictive model based on quantum mechanics calculation, and thus does not suffer from the problem of missing binary parameters. It has been successfully used to screen IL solvents with desired properties in a large search space (Lee and Lin, 2015). In this method, ILs are always defined as an ion pair, rather than individual functional descriptors used in group contribution (GC) method, which makes it hard to be directly integrated into the CAILD framework. Moreover, when using the COSMO-SAC model to predict thermodynamic properties, a ready COSMO database containing all molecular information is required, which means new compound not included in its database cannot be designed by this method. Therefore, an approach taking the advantage of COSMO-SAC model and providing fast and reliable generation of σ-profiles and cavity volumes (V_{COSMO}) of general compounds for solvent design is strongly needed. For this purpose, Mu et al. (2009) developed a group contribution based theory named GC-COSMO. However ILs are not included and applicable.

In this work, an extended GC-COSMO method is presented to predict the σ-profile and V_{COSMO} of ILs, which are further used for COSMO-SAC calculation. The approach is then incorporated into a CAILD framework structured by multi-scale simulations of physical properties of compound, thermodynamics of system, performance of process, constraints and optimization of design problems. The optimal IL solvent is acquired by solving a mixed-integer nonlinear programming (MINLP) problem with a deterministic algorithm. Two separation tasks of benzene–cyclohexane extraction and post-combustion carbon dioxide (CO_2) capture are tested as example.

2. Description of the methodology

The strategy of the presented CAILD methodology is illustrated in Fig. 1. At the beginning, a database covering the information of σ-profile, V_{COSMO}, group classification, valance of all IL groups, and parameters for physical predictions is acquired. Then the thermodynamics of the system with candidate ILs are calculated by the COSMO-SAC model, and the physical properties are predicted based on semi-empirical models. After that, separation process performance, such as selectivity (S), capacity (β) and performance index (PI) for extraction, or Henry's law constant ($H_{i/S}$) as well as solubility (x_i) for absorption are obtained. After the forward establishment of the links between IL structures and various process properties, reverse design of IL solvents that own the optimal target properties within the constraints can be implemented. Each design task is formulated as an MINLP problem and solved by branch and bound (BNB) algorithm.

2.1. GC-based σ-profile estimation method

2.1.1. Calculation of the σ-profile

In the COSMO-SAC model (Lin and Sandler, 2002; Wang et al., 2007), molecular interactions are calculated from the interaction between the screening charges on surfaces when the molecules are in close contact. Because the pairwise interaction between segments is based on contact surfaces of the identical size, a