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# Optimal design of ionic liquids for thermal energy storage

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ABSTRACT

Ionic liquids (ILs) are an emerging group of chemicals which, with their tunable physicochemical properties, exhibit promise for use as novel materials in many applications. Thermal (e.g. solar) energy storage (TES) is one such area where they show potential to be thermally stable at high temperatures and store high amount of heat energy. A large number of ILs, through the combination of different cations and anions, can be potentially synthetized thereby presenting a good platform for design. However, since it is not possible to study this large number of compounds experimentally it is necessary to use computational methods to evaluate them. In this article, we present a computer-aided framework to design task-specific ionic liquids (ILs), using structure- property models and optimization methods. Thermal energy storage density (capacity) was used as a measure of the ability of an IL to store thermal (solar) energy. An hydroxyl functionalized imidazolium-based IL, [3-hydroxy-imidazolium]$^{+}$[BF4]$^{-}$, was found to be the optimal candidate with highest thermal energy storage capacity along with appropriate melting point and decomposition temperature.



## 1. Introduction

Advancements in solar trough and solar tower technologies have enabled concentration of thermal energy to the extent that it can be used to drive traditional steam cycles providing an alternative to fossil fuel use (MacFarlane et al., 2014). Therefore, harvesting solar energy using arrays of parabolic trough collectors will enable generation of electricity at a large scale. In solar power plants, thermal energy storage (TES) is necessary to extend production periods of low or no sunlight. An important component of TES systems is thermal fluid which is needed to transfer and store heat for relatively short periods. A parabolic trough system typically consists of a series of collectors that are big mirror-like reflectors used to concentrate solar energy. When the solar radiation is received by these collectors the reflected light is concentrated at the center of the collector. A heat transfer fluid (HTF) passed through tubes present at the center of the collector absorbs the accumulated heat. The collected thermal energy is then transferred from the HTF to a storage medium or is stored in a reservoir using the heat capacity of the HTF itself (Moens et al., 2003). The storage media can then release the thermal energy when needed for further conversion to electrical energy. Thermal energy storage (TES) therefore makes solar energy a more reliable and economic alternative source of energy.

Fluids that have high potential to store heat energy such as thermal oil (e.g. VP-1$^{TM}$), or nitrate salts (e.g. HITEC-XL$^{TM}$) are suitable for thermal energy storage applications. However, nitrate salts have melting points (freezing point) above 200 °C while mineral oils have upper temperature limit of 300 °C (Moens et al., 2003) thus limiting their use to a narrow temperature range and thereby reducing the overall efficiency of the process. Ionic liquids (and salts) have properties that are ideal for thermal storage applications. These attractive properties include high heat capacity, high decomposition temperature and relatively high density at operating conditions. Ionic liquids (ILs) are a new generation of materials that have a wide range of applications (Rogers and Seddon, 2003). Similar to salts ILs are composed of ions but have much lower melting points. Several ILs are in liquid state at room temperature (commonly referred as room temperature ionic liquids [RTILs]). ILs consist of an organic cation (a cation core with alkyl side chains) and a charge-delocalized inorganic or organic anion (Armand et al., 2009). They usually possess good thermal stability (i.e. high decomposition temperature) making them appropriate for processes operating at high temperatures. Ionic liquids can be customized (e.g. Gao et al., 2015) through appropriate selection of cations, anions and alkyl side chain groups attached to the cation. Therefore, ILs can be tuned to impart specific functionalities (e.g. Seo et al., 2014) for a given application by changing cation/anion/cation side chain groups.

In this study, we focus on the computational design of optimal ionic liquids with high thermal storage density for solar energy

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storage applications. The key requirements of a thermal storage medium include high thermal storage capacity ($\rho \times Cp$ [MJ/m$^3$ K]), high thermal stability (MacFarlane et al., 2014), and a wide liquid range. Therefore the properties of ionic liquid that need to be optimized for thermal storage applications include: density, heat capacity, thermal decomposition temperature and melting point. Heat capacity measurements of diverse ionic liquids reveal wide ranging values (Paulechka, 2010). The melting point of ionic liquids can be easily adjusted by the choice of cation type, anion or the groups attached to the side chains of the cation core. Thermal stability and other thermal and physical properties of ILs have been previously studied (Nishikawa et al., 2007; Diedrichs and Gmehling, 2006; Wilkes, 2004; Zhang et al., 2006; Crosthwaite et al., 2005; Tenney et al., 2014). It has been widely reported that many ionic liquids have high thermal decomposition temperatures. In order for us to find the optimal ionic liquid structure having desired melting point and decomposition temperature as well as maximum thermal storage capacity, thousands of different IL structural combinations need to be evaluated. Since this is not feasible experimentally, a computer-aided approach is suggested in this paper.

Computer-aided molecular design (CAMD) is a technique that has been widely used to design molecular compounds for different applications (Brignole et al., 1986; Camarda and Maranas, 1999; Achenie et al., 2003; Karunanithi et al., 2006; Folić et al., 2007; Samudra and Sahinidis, 2013b; Stavrou et al., 2014). Gani and Brignole (1983) initially conceptualized this method to screen solvents based on UNIFAC group contribution approach. CAMD usually integrates structure based property prediction models (e.g. group contribution models) and optimization algorithms to design molecular compounds with desired properties. More recently, this approach has been extended to the design of ionic liquids (McLeese et al., 2010; Roughton et al., 2012; Karunanithi and Mehrkesh, 2013; Chong et al., 2015; Hada et al., 2015). A comprehensive framework for computer-aided ionic liquid design (CAILD) was recently published by our group (Karunanithi and Mehrkesh, 2013). Key to the successful development and use of CAILD methods is the availability of predictive models for the properties of interest. In this work we present a new CAILD model to design novel ionic liquids as thermal fluids for thermal (solar) energy storage applications. This CAILD model utilizes existing group contribution methods to predict physical and thermal properties of ILs. By considering a structurally diverse set of building blocks we are able to demonstrate that new and novel structural variants of ILs can be tailored specifically for this application.

## 2. Formulation of the design problem

In this section, we focus on presenting a computer-aided ionic liquid design (CAILD) model, as shown generically in Fig. 1, to find/design an optimal ionic liquid with high thermal storage capacity (highest among the candidates which were considered in this study) while having a reasonably low melting point and a decomposition temperature higher than the maximum operating temperature of a solar energy storage system.

In this method a variety of cation cores, cation side chain groups (including certain functional groups such as OH), and anions were selected as ionic liquid building blocks. Typical CAILD approach requires solution to the forward problem (i.e. property prediction) as well as the reverse problem (i.e. structure generation). In a mathematical programming based CAILD approach, the generic CAILD problem shown in Fig. 1, is converted into a mathematical programming model. Here, the physical properties of ionic liquids are estimated using structure based predictive models such as group contribution (GC) models (forward problem) and optimal ionic liquid structures are generated by solving a mixed-integer non-linear

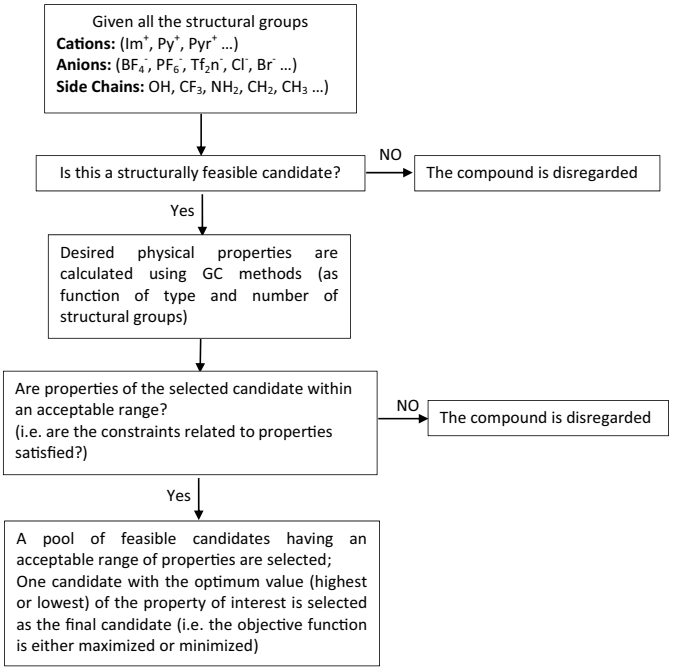


**Fig. 1.** A general scheme of a CAILD problem.

programming (MINLP) formulation of the design problem (reverse problem). In this study, existing group contribution (GC) methods for prediction of the physical properties of interest, namely, density, heat capacity, melting point and decomposition temperature, were used (Valderrama and Zarricueta, 2009; Valderrama and Rojas, 2009; Valderrama et al., 2011a,b; Lazzús, 2012a,b). The CAILD framework proposed by Karunanithi and Mehrkesh (2013) was utilized to formulate the thermal storage fluid (TSF) design problem as an MINLP model. Structural constraints (Eqs. (1)–(5)) adopted from our previous work were utilized again to design structurally feasible ionic liquids. These constraints are a sub-set of a comprehensive set of structural constraints presented in Karunanithi and Mehrkesh (2013).

Linear physical property constraints based on GC predication (Eqs. (11)–(15)) were integrated with the structural feasibility constraints. The objective of the design problem was to identify the optimal ionic liquid structure that has the highest thermal storage capacity. Therefore, the objective function was formulated to maximize the product of density and heat capacity of the ionic liquid. The solar thermal storage process is typically carried out at a temperature of around 300 °C. Therefore, the thermal storage fluid – in this case the designed ionic liquid – should be operable at temperatures slightly above 300 °C. To ensure that the ionic liquid does not decompose during the process, we enforce a constraint on thermal decomposition temperature to be above 400 °C (Eq. (24)). The temperature of ionic liquid after energy exchange should be higher than its melting point. To ensure this, a constraint on melting point to be lower than 140 °C is imposed (Eq. (25)). The temperature window between melting point and decomposition temperature is the range at which the process can operate. The basis set (the structural building blocks) considered for this problem includes 5 cation cores, 9 anions and 5 cation side chain groups (alkyl and functional groups) which are shown in Table 1. This selection was based on groups for which group contribution parameters were available for all the properties of interest. A general formulation of the thermal storage fluid CAILD model is shown below.

*Objective function*

$$f_{obj} = \max(\rho \times C_P)$$