

Ionic Liquid Design for Enhanced Carbon Dioxide Capture – A Computer Aided Molecular Design Approach

Fah Keen Chong^{*a}, Fadwa T. Eljack^b, M. Atilhan^b, Dominic C.Y. Foo^a,
Nishanth G. Chemmangattualappil^a

^aDepartment of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham Malaysia Campus, Jalan Broga, 43500 Semenyih, Selangor, Malaysia.

^bDepartment of Chemical Engineering, College of Engineering, Qatar University, PO Box 2713, Doha, Qatar.
kebx3cfe@nottingham.edu.my

Greenhouse gases emission is known as the main factor of climate change, and carbon dioxide (CO₂) makes up vast majority of them. Carbon capture and storage (CCS) is a vital technology to mitigate industrial CO₂ emissions, which is mainly generated in power plants. Currently, post-combustion capture based on aqueous amine scrubbing is considered as the most suitable technology for CO₂ capture. However, the use of amine for CO₂ capture has some disadvantages, such as high energy required for solvent regeneration, high solvent loss, and degradation of solvent. Recently, ionic liquids (ILs) are considered as potential alternative, because they have negligible vapour pressure, and high thermal stability. In addition, through matching of cations and anions, ILs provide a flexibility to tune their properties. However, due to vast number of potential ILs, time and expense required to obtain the optimal ILs for CO₂ absorption through experimentation is unaffordable. This work presents a Computer-Aided Molecular Design (CAMD) approach for the design and selection of optimal ILs specifically for the purpose of CO₂ capture. The approach utilises group contribution method to estimate the thermophysical properties of ILs, by considering the structural constraints and allowed combination of cations and anions. Predicted properties of the potential candidates are in good agreement of experimentally measured properties.

1. Introduction

The International Energy Agency (IEA) reported that the global energy demand is projected to grow to 16,730 million tonnes oil equivalent (toe) in 2035, i.e. more than one-third based on the figure in 2010 (IEA, 2012). Despite the growth in low carbon energy sources, fossil fuels remain dominant in the global energy mix, mainly due to the subsidies that are six times more than that for renewables (IEA, 2012). Closely related to the issue with energy use is the deterioration of environmental quality. Carbon dioxide (CO₂) concentration in the atmosphere has exceeded 400 ppm in May 2013 for the first time in history (IEA, 2013). In the IEA's perspective, energy is the core of the problem, since fossil fuels accounts for 80 % of global energy consumption, and hence contributes approximately two-thirds of the global GHG emissions (IEA, 2013). A possible solution is to use a mix of several "technological wedges" in order to cut emissions to the desired targets (Pacala and Socolow, 2004). One of the "wedges" that receives good attention worldwide in recent years is carbon capture and storage (CCS) technologies, which can capture CO₂ from large point sources, such as power plants and petrochemical complexes.

At the moment, there are four known technologies for carbon capture, namely post-combustion, pre-combustion, oxy-fuel combustion, and chemical looping combustion. Among all, post-combustion capture based on aqueous amine scrubbing is currently the most implemented because it can be installed to the existing power plants and gas processing facilities with minimal modification to the plants. Monoethanolamine (MEA) is the most commonly used solvent for CO₂ absorption. However, there are doubts about the rate of degradation in oxidising environment of flue gases, solvent loss due to high vapour pressure, and high energy required for desorption when MEA is used (Olajire, 2010). Ionic liquids (ILs) have recently been introduced as green solvents for different applications, for example gas

purification (Brennecke and Maginn, 2003) and biomass fractioning (Liebmann et al., 2012). Their unique combination of properties, for example large liquid phase range, negligible vapour pressure, high thermal stability, and excellent solvation properties for a variety of materials, makes them excellent alternative to conventional organic solvents. ILs are also called “designer solvents”, because of their thermophysical properties that can be tuned accordingly, by switching cations and anions. Therefore, it is possible to design specific ILs for a particular application. However, it is estimated that at least 10^6 unique combinations of cation and anion exist and they can be easily prepared in laboratories (Plechkova and Seddon, 2008). It is very challenging task to determine the suitable ionic liquid for a specific job, merely through trial-and-error approach. Hence, there is need for a systematic approach to identify a subset of IL candidates prior to testing experimentally.

Computer-aided molecular design (CAMD) approach is a very useful method that has been widely applied to design task-specific organic solvents, such as liquid extraction (Gani and Brignole, 1983), gas absorption (Buxton et al., 1999), and crystallisation (Karunanithi et al., 2006). It is an approach to reverse engineer molecular structure of organic solvents, by estimating property using property prediction models and optimisation algorithm. Recently, there are works done on synthesising novel ILs structure through CAMD. Matsuda et al. (2007) first presented the design of ILs, based on quantitative structure property coupled with descriptor of group contribution. Tian et al. (2009) proposed to use quantum chemical calculation to design novel ILs as green electrolytes. McLeese et al. (2010) compared the use of deterministic algorithm and heuristic algorithm in ILs design problem. Billard et al. (2011) showed the possibility of designing new novel ILs, prior to synthesis of designed ILs and experimental test. Chávez-Islas et al. (2011) later presented a mixed-integer nonlinear programming (MINLP) formulation for the optimal molecular design of ILs to recover ethanol from ethanol-water system. Roughton et al. (2012) and Valencia-marquez et al. (2012) presented integrated process-product design of ILs for azeotrope separation via extractive distillation. Hada et al. (2013) proposed a methodology combining characterisation based group contribution method (GCM), chemometric and property clustering technique in ILs design. Recently, Karunanithi and Mehrkesh (2013) presented a general CAMD framework specifically for ILs, based on semi-empirical structure-property models and optimisation methods. The difference between mentioned works and the present one is that different structural constraints are applied. Common structural constraints used for organic solvent design are employed here, together with other considerations for cations and anions selection.

This paper presents a MINLP model to determine optimal design of IL for CO₂ absorption purpose, with an illustrative example. The paper is outlined as follows: A formal problem statement is described in the next section, followed by the modelling of constraints. Formulated MINLP problem is shown, then results are discussed. Finally, conclusions and future works are given at the end of this paper.

2. Problem Statement

The paper addresses the following: Given a set of pre-selected IL cations and anions, it is desired to design a set of suitable/optimal ILs that maximise CO₂ absorption. The cations and anions are selected based on gas absorption performance (Baltus et al., 2004) and separation performance of IL (Cadena et al., 2004). Table 1 shows the groups of cations, anions, and organic functional groups considered for this example. In this example, only pure IL is considered, i.e. mixture of ILs will not be selected.

Table 1: Cations, anions and organic functional groups considered

Type	k	Groups	Type	k	Groups
Organic	1	CH ₃	Anion	5	[BF ₄] ⁻
	2	CH ₂		6	[PF ₆] ⁻
	3	CO ₂		7	[Cl] ⁻
Cation	4	[Mim] ⁺			

3. Modelling of Constraints

3.1 Property constraints

In IL solvent design formulations, viscosity is an important property because it will affect the IL affinity to capture CO₂. Viscosity also affects the power required for pumping the solvent within the system, and the subsequent operating cost. Therefore, viscosity of IL is included in this model. To compute the viscosity of IL, Orrick-Erbar-type approach is adapted, which employs GCM (Gardas and Coutinho, 2008a). The proposed approach is shown below:

$$\ln \frac{1,000\mu}{\rho M} = A + \frac{B}{T} \quad (1)$$

where μ is IL viscosity in Pa.s, ρ is IL density in g cm^{-3} , M is IL molecular weight, and T is the system temperature in K. Parameters A and B are estimated as follows:

$$A = \sum_k v_k A_{k,\mu}; \quad B = \sum_k v_k B_{k,\mu} \quad (2)$$

where v_k is the number of group k , $A_{k,\mu}$ and $B_{k,\mu}$ are contributions of group k to parameters A and B , respectively. The IL density is determined using equation below.

$$\rho = \frac{M}{NV(a + bT + cP)} \quad (3)$$

Eq(3) is the group contribution model for IL density developed by Ye and Shreeve (2007), which was extended by Gardas and Coutinho (2008b). P is the system pressure, N is the Avogadro constant, given as 0.6022 , V is the molecular volume in \AA^3 , the coefficients a , b and c were estimated as 0.8005 , $6.652 \times 10^{-4} \text{ K}^{-1}$ and $-5.919 \times 10^{-4} \text{ MPa}^{-1}$ respectively.

3.2 Process constraints

Gas absorption processes involve two phases (gas and liquid), thus equilibrium relationships are considered in the model. Due to extremely low vapour pressure of ILs, no IL is assumed to be present in vapour phase. However, the liquid phase forms a non-ideal liquid mixture, due to the presence of organic and ionic compounds. The nonideality will be modelled through activity coefficient γ_i , as shown in the Eq(4).

$$y_i P \varphi_i(T, P, y_i) = x_i \gamma_i P_i^S \quad (4)$$

Eq(4) describes the gas-liquid equilibrium at low pressure, where x_i and y_i are the mole fractions of component i in liquid and gas phases respectively, P_i^S is the saturated vapour pressure of component i , and $\varphi_i(T, P, y_i)$ is the gas-phase fugacity coefficient. Activity coefficient can be estimated using UNIFAC model, which combines the functional group concept with a model based on an extension of the universal-quasi-chemical theory (UNIQUAC) of liquid mixtures. By decomposing IL into simple functional groups, UNIFAC model can be applied to determine the activity coefficient of ILs (Lei et al., 2009). To adapt the model proposed by Lei et al. (2013), ILs are divided into a main skeleton of cation and anion, and the alkyl chain is decomposed into separate CH_2 or CH_3 groups. UNIFAC model is a well-established technique for activity coefficient estimation and is given as follows:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (5)$$

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - 5q_i \left[1 + \frac{V_i}{F_i} + \ln \left(\frac{V_i}{F_i} \right) \right] \quad (6)$$

$$F_i = \frac{q_i}{\sum_j q_j x_j}; \quad V_i = \frac{r_i}{\sum_j r_j x_j} \quad (7)$$

$$r_i = \sum_k v_k^{(i)} R_k; \quad q_i = \sum_k v_k^{(i)} Q_k \quad (8)$$

$$\ln \gamma_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (9)$$

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \left(\theta_m \psi_{km} / \sum_n \theta_n \psi_{nm} \right) \right] \quad (10)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}; \quad X_m = \frac{\sum_i v_m^{(i)} x_i}{\sum_i \sum_k v_k^{(i)} x_i} \quad (11)$$

$$\psi_{nm} = \exp[-(a_{nm}/T)] \quad (12)$$

To enforce that the vapour and liquid mole fractions always equal to unity, the mole fraction summation constraints for both phases are included.

$$\sum_i y_i = 1 \quad (13)$$

$$\sum_i x_i = 1 \quad (14)$$

4. Optimisation Model

The optimisation objective is to select the optimal IL which is able to absorb the highest amount of CO₂:

$$\max x_1 \quad (15)$$

In the objective function, x_1 stands for the liquid mole fraction of CO₂, which is also the amount of CO₂ absorbed by selected IL. Therefore, the objective function simply states the target is to obtain highest recovery of CO₂ by choosing suitable IL. In this illustrative example, the selectivity of other gases over CO₂ is ignored, i.e. only CO₂ will be absorbed by selected IL. Eq(16) is included to ensure only one cation and one anion should be selected.

$$\sum_m \alpha_m = 1; \quad \sum_n \beta_n = 1 \quad (16)$$

where α_m and β_n are the binary variables representing each cation m and each anion n , respectively. CH₃ groups present in the cation of the selected IL should be quantified and added to the UNIFAC model calculation. Therefore, the equation below is included.

$$g_{CH_3} = \sum_m G_{CH_3,m} v_m \alpha_m \quad (17)$$

where g_{CH_3} is the number of CH₃ groups in the selected cation, $G_{CH_3,m}$ is the number of CH₃ group in the individual cation structure. In organic solvents design problem, valence and octet rules are considered. In this work, IL is decomposed into electrically neutral group, similar to other organic functional groups. Therefore, same considerations are included in the model, i.e. IL chosen should have a complete structure with no free bond, and the following constraints should be obeyed.

$$\sum_k v_k \geq 2 \quad (18)$$

$$\sum_k n_k v_k - 2 \left(\sum_k n_k - 1 \right) = 0 \quad (19)$$

where n_k is the available free bond of group k .

5. Optimal Molecular Design

For this design problem, system temperature and pressure are set at 323.2 K and 0.7 MPa. In order to minimise pumping costs and increase mass transfer rates, low viscosity of IL is desired (Gardas and Coutinho, 2008a). However, ILs are reported to have relatively higher viscosities compared to those of common organic solvents. Organic solvents generally have viscosity of about 0.0002 to 0.01 Pa.s; while ILs viscosity span a larger range of 0.01 to 100 Pa.s (Bonhôte et al., 1996). A constraint is added to ensure that viscosity of chosen IL is not affecting the energy costs significantly, and it reads as:

$$\mu \leq 0.1 \quad (20)$$

In this example, the length of alkyl chain that can be attached to the cation is no more than twelve carbon. This is just an arbitrary number. However, it should be limited by the availability of selected cation with this chain length or ability in synthesising such cation.

$$\sum_k v_k \leq 12 \quad k = 1, 2 \quad (21)$$

The MINLP model presented in this work is based on group contribution type of property prediction models. This model is solved using LINGO version 10. Five ILs were determined by doing integer cuts, and the optimal results are shown in **Error! Not a valid bookmark self-reference..**

Table 2: Optimal IL molecular design results

IL chosen	Predicted solubility, x_1	Molecular weight, $M(\text{g mol}^{-1})$	Predicted density, $\rho (\text{g cm}^{-3})$	Predicted viscosity, $\mu (\text{Pa.s})$	Experimental solubility	Relative deviation, RD (%)	Reference
[C ₉ mim][BF ₄]	0.116	296.2	1.074	0.092	-	-	-
[C ₈ mim][BF ₄]	0.108	282.1	1.091	0.077	0.101	7.37	(Gutkowski et al., 2006)
[C ₇ mim][BF ₄]	0.1002	268.1	1.110	0.065	-	-	-
[C ₆ mim][BF ₄]	0.0914	254.1	1.133	0.054	0.103	11.61	(Costantini et al., 2005)
[C ₅ mim][PF ₆]	0.091	298.2	1.308	0.094	-	-	-

The results show that CO₂ absorbed by IL increases with increasing number of carbon in alkyl chain attached to cation, the same trend is observed for IL viscosity. This agrees with a literature study done on solubility of CO₂ in a series of imidazolium-based ILs (Baltus et al., 2004). The relative deviation of CO₂ solubility between experimental data and predicted values are shown in Table 2. The difference is mainly due to small errors in the chosen prediction models. The proposed approach is able to design novel IL for CO₂ absorption, according to the required specifications or performance by the industry.

6. Conclusions

CAMD approach, which is commonly used for molecular design of organic compounds, is presented here to design optimal IL specifically for CO₂ absorption. The formulated MINLP model determines the optimal IL which is able to absorb the highest amount of CO₂, considering relevant properties and structural constraints. The model presented in this work is based on group contribution type of properties predictive models, and thus limited by the availability of group contribution data for cation and anion groups. Future works should include selectivity of CO₂ relative to other gases, mixture of ionic liquids, and integrating optimisation model with newly available experimental data.

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