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Ionic Liquid Mixture Design for Carbon Capture using Property Clustering Technique

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Ionic liquids (ILs) have recently been introduced as green solvents and potential substitute to volatile organic compounds. This is due to their negligible vapour pressure, high thermal stability, and large liquid phase range. Moreover, their physical and chemical properties can be tuned accordingly by proper choice of cations and anions. Thus, researchers suggest replacing conventional amine based carbon dioxide (CO_2) capturing solvents with IL solvents. However, study shows that ILs with high absorption rate and capacity generally have relatively higher viscosity and cost, which make pure IL solvent impractical. Instead, a mixture of ILs is desired to improve the overall performance as a CO_2 solvent. Given there are up to 10^{12} possible binary mixtures, it is time consuming and expensive to identify suitable binary IL mixture as CO_2 capturing solvent by experimental approach. The main focus of this work is to develop a systematic property based visual approach to synthesis IL binary mixtures, specifically for carbon capture purpose. An illustrative case study is solved to demonstrate the proposed approach.

1. Introduction

Carbon dioxide (CO_2) emission has become a major issue faced by the society, and energy is the core of the problem when fossil fuels remain dominant in the global energy supply (IEA, 2013). A potential solution to this problem is through carbon capture and storage (CCS), where CO_2 is separated from emission sources and stored in secure geological storage. Post-combustion capture using amine based solvents is currently the most implemented CO_2 capture technology, but these solvents possess some drawbacks, such as solvent loss, solvent degradation, and high energy consumption for solvent regeneration. Ionic liquids (ILs), which are regarded as green solvents, have been suggested as possible substitute for conventional amine based solvents. ILs have a very unique combination of properties, including negligible vapour pressure, wide liquid phase range, and high thermal stability (Qureshi et al., 2013). Besides, their properties can be tailored to suit a specific task by switching the cations and anions, and hence ILs are also named “designer” solvents. Hence, it is possible to design pure ILs to specifically absorb CO_2 from flue gas. However, according to Wang et al. (2013), ILs with high CO_2 absorption rate and capacity are relatively more expensive and have higher viscosities. In this case, a mixture of ILs can be used as solvent, to ensure the CO_2 solubility remains high, while viscosity and cost are acceptable as well. There are approximately 10^{12} possible binary mixtures of IL (Holbrey and Seddon, 1999), which makes the identification of suitable IL mixture for CO_2 capture through experiment time consuming and costly.
Different techniques have been reported to solve organic compound mixture design problem. Klein et al. (1992) presented a methodology to determine the identity and composition of solvent mixtures, by integrating optimisation algorithm and computer aided mixture design. Similarly, Duvedi and Achenie (1997) presented mathematical programming model to design environmental friendly refrigerant mixtures. This model includes binary variables to identify number and type of refrigerant constituents in mixture, and continuous variables to determine properties of mixture. Sinha et al. (2003) also proposed to design blanket wash solvent mixtures that meet thermophysical property requirements and environmental

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restrictions by using interval analysis. Conte et al. (2011) developed a systematic approach to design liquid formulated products, including liquid mixtures. This approach is an integration of computer-aided model based techniques with heuristic based experimental testing and improvement of designs of liquid formulated products. Yunus et al. (2012) also proposed to design tailor-made mixture products through three stages approach, which includes product design, product identification, and experimental verification. Papadopoulos et al. (2013) presented two-steps methodology to synthesise binary working fluid mixture for Organic Rankine Cycles. The optimum mixture performance targets are first identified by designing first pure component of the mixture, followed by designing the required matching component and the optimum mixture concentration. However, the above mentioned works are based on mathematical programming techniques. These techniques do not provide insights of the problem that can be helpful to user without mathematical optimisation background. In addition, mathematical programming generally includes nonlinear property prediction models, which increase the complexity of the approach and lead to sub-optimal solutions. To overcome these drawbacks, Solvason et al. (2009) proposed to design mixture of organic compounds by using property clustering technique, where the design problem can be visualised on ternary diagram.

To date, there is no work reported addressing IL mixture design problem, using either mathematical programming or visual approach. Thus, a property based visual approach is introduced in this work to design IL mixture specifically for CO_2 capture purpose, by using property clustering technique and group contribution (GC) method. A case study involving five new experimentally tested ILs is solved to demonstrate the proposed approach.

2. Property Clustering

Property clustering was first developed to represent and track properties in process streams following a conserved manner (Shelley and El-Halwagi, 2000). This technique was then extended by Eljack et al. (2006) to solve molecular design problems, by introducing molecular property operators. This technique allows for simple linear additive rules of the groups, as shown in Eq(1).

$$\psi_j\left(P_j\right) = \sum_{i=1}^{u} x_i \psi_j\left(P_{ji}\right) \tag{1}$$

In Eq(1), $\psi_j(P_j)$ is the property operator of the j^{th} property, $\psi_j(P_{ji})$ is the property operator of the j^{th} property of IL constituent i, x_i is the mole fraction of IL constituent i, and u is the total number of IL constituents. According to this equation, property operator follows simple linear mixing rules, regardless of the linearity of the raw property. Property operator can then be converted into property clusters using Eq(2) (Eden et al., 2004).

$$\Omega_{ji} = \frac{\psi_j\left(P_{ji}\right)}{\psi_j^{ref}\left(P_j\right)}, \qquad AUP_i = \sum_{j=1}^{P} \Omega_{ji}, \qquad C_{ji} = \frac{\Omega_{ji}}{AUP_i} \tag{2}$$

where Ω_{ji} is normalised property operator for property j of constituent i, $\psi_j^{ref}(P_j)$ is reference operator of j^{th} property, AUP_i is augmented property (AUP) index of constituent i, and C_{ji} is property cluster for property j of constituent i.

3. Visualisation of the Problem

By using property clustering technique, the IL mixture design problem can be visualised in a ternary diagram, where pure property cluster is represented by each vertex in the diagram. Although the number of clusters is limited to three for visualisation purpose, the number of properties considered during design can be more than three. On top of that, properties with no group contribution prediction models can also be included for screening purpose, if there are appropriate prediction models for these properties. All designed IL mixtures should have properties fulfilling all property constraints. Property constraints for all properties included in ternary diagram are represented as a feasibility region defined by six unique points (El-Halwagi et al., 2004). The following design and optimisation rules have been developed referring to those previously suggested by Eden et al. (2004) and Eljack and Eden (2008) to ensure the designed IL mixtures are valid solution.

Rule 1: When two IL constituents, I_1 and I_2, are added linearly on the diagram, the AUP values and distance between them provide information of I_1-I_2 mixture.

Rule 2: More constituents can be added if the sum of all constituent fractions is not equal to one.

Rule 3: The final summation of all constituent fractions must be one.
Rule 4: The fraction of each IL constituent chosen as part of the mixture must be between zero and one.
Rule 5: The cluster value of the designed IL mixtures must be located within the feasibility region on the ternary diagram.
Rule 6: The AUP values of the designed IL mixtures must be within the range of target AUP, which are determined from the six point bounding. If the AUP value is outside the range of target AUP, the IL mixture is not a feasible solution.
However, this is an IL binary mixture design problem, the following rule should be included.
Rule 7: Number of constituents occurs in the IL mixture is limited to two only.
If properties with no available GC prediction models are considered, these properties must be determined for each designed IL mixture by using appropriate prediction models. The calculated values of these properties must be within the targeted range as well, for the designed mixture to be a valid solution.

4. Case Study

An illustrative case study is solved to demonstrate the propose approach. Table 1 shows the five IL constituents considered in this design problem, along with their respective properties. The main objective is to determine a list of potential IL binary mixtures for carbon capture purpose. In this IL mixture design problem, the three properties considered are density (ρ), viscosity (μ), and solubility of CO_2 (S), which are denoted as C_1, C_2, and C_3 respectively in ternary diagram. These five ILs considered in this case study were tested through experimental lately to obtain the density and CO_2 solubility of each pure IL. The density and CO_2 solubility data is obtained at temperature of 303.15 K and pressure of 700 kPa. The viscosities of these ILs are taken from literature since the data are widely available. The GC prediction model for density is shown in Eq(3), where x_i is the fraction of IL constituent i and ρ_i is the density of each IL constituent in kg/m^3.

$$\rho = \sum_i x_i \left(\frac{1}{\rho_i} \right) \tag{3}$$

To estimate viscosity of IL mixture, Refutas method is applied in this work, where viscosity-blending index, *VBI* is determined for each IL constituent (Maples, 2000).

$$VBI_i = 10.975 + 14.535 \ln\left[\ln\left(\nu_i + 0.8\right)\right] \tag{4}$$

$$\mu_i = \nu_i \rho_i \tag{5}$$

$$VBI = \sum_i x_i VBI_i \tag{6}$$

where VBI_i is the viscosity-blending index of IL constituent i, ν_i is the kinematic viscosity of IL constituent i in m^2/s, and μ_i is the dynamic viscosity of constituent i in kg/(m.s). As for solubility of CO_2 in IL mixture, linear mixing rule is applied as described in Eq(7), where S_i is the CO_2 solubility of constituent i in mol CO_2/mol IL.

$$S = \sum_i x_i S_i \tag{7}$$

Table 1: IL constituents considered

IL	*i*	Density, ρ (kg/m^3)	Viscosity, μ (kg/(m.s))	Solubility of CO_2, *S*
[BMIm][NTf_2]	1	1,434.6	0.0440 (Hyun et al., 2002)	0.1714
[N4111][NTf_2]	2	1,389.8	0.1051 (Bhattacharjee et al., 2014)	0.1809
[DEMA][OMs]	3	1,132.3	0.1300 (Merkel et al., 2014)	0.0841
[DEMA][OTf]	4	1,288.0	0.0317	0.1050
[N1888][NTf_2]	5	1,095.0	0.4034 (Fröba et al., 2008)	0.3138

Table 2 shows the target property ranges for this IL mixture design problem. Designed IL mixtures should possess similar properties as current conventional CO_2 solvents (i.e. ethanolamines) (Chong et al., 2014). Thus, the ranges of target properties are set according to the properties of ethanolamines (The Dow Chemical Company, 2003). Viscosity of designed IL mixtures should be as low as possible to minimise pumping power required to circulate the solvent within the process. Hence, the target range of viscosity is set to be between 0.01 to 0.20 kg/(m.s) (Bonhôte et al., 1996). Solubility of CO_2 for designed solvent should be at least as good as the conventional solvent. Therefore the boundary is set to between 0.09 and 0.40 mol CO_2/mol solvent (Zhang et al., 2012). Using the proposed approach, the problem can be visualised and it is shown in Figure 1. The dotted lines in Figure 1 represent the feasibility region based on the target property ranges in Table 2. The maximum and minimum AUP are determined to be 2.533 and 5.667 from the boundaries.

Ten IL mixtures are formulated as potential CO_2 solvents using the proposed approach, and the results are shown in Figure 2. The AUP values of these candidates are also determined and shown in Table 3, where all are within the range of AUP. The properties of all IL mixtures are back calculated and included in Table 3. These designed IL mixtures fulfil all the property constraints shown in Table 2. From the results, a mixture of 0.5 mol of [N4111][NTf_2] and 0.5 mol of [N1888][NTf_2] yields the highest CO_2 solubility among all ten mixtures. This is expected because both ILs have the highest CO_2 solubility as pure ILs. According to Table 3, it is noted that all designed IL mixtures have properties in between those of their precedents. This means that CO_2 solubility of IL mixtures cannot be higher than pure ILs, but the viscosity will be lower, and hence more acceptable in overall.

Table 2: Target property ranges to design IL mixtures for carbon capture purpose

Property	Lower bound	Upper bound
Density, ρ (kg/m^3)	1,000	2,000
Viscosity, μ (kg/(m.s))	0.01	0.20
Solubility of CO_2, S	0.09	0.40

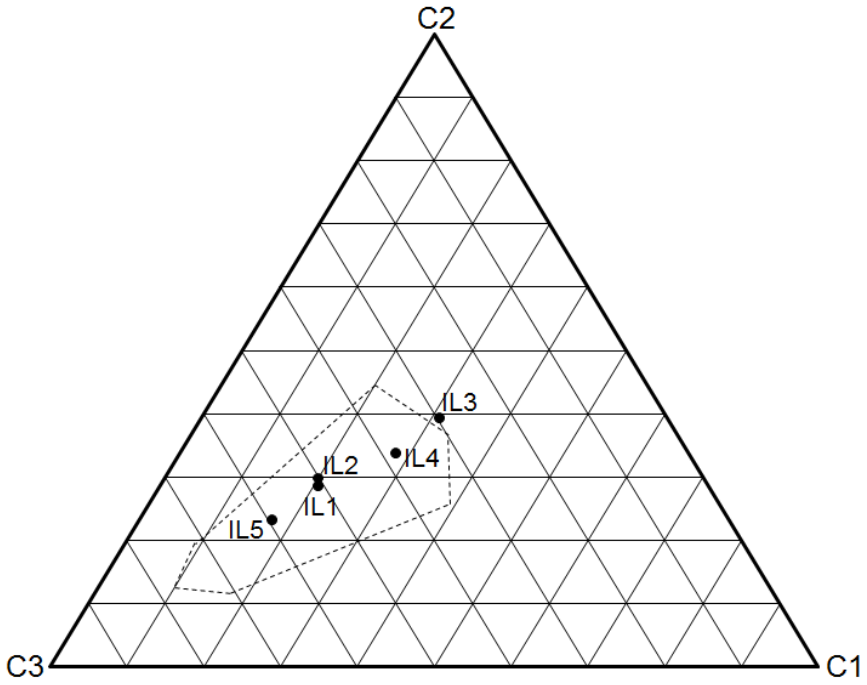

Figure 1: Ternary diagram representing visualisation of IL binary mixture design problem

Table 3: Results of IL binary mixture design problem

IL mixture	IL constituents	ρ (kg/m^3)	μ (kg/(m.s))	S	AUP
1	0.5 mol I_1 + 0.5 mol I_2	1,411.4	0.0333	0.1761	3.4910
2	0.5 mol I_1 + 0.5 mol I_3	1,265.3	0.0446	0.1277	3.1109
3	0.5 mol I_1 + 0.5 mol I_4	1,356.9	0.0202	0.1382	3.0692
4	0.5 mol I_1 + 0.5 mol I_5	1,241.6	0.0729	0.2426	4.3275
5	0.5 mol I_2 + 0.5 mol I_3	1,247.9	0.0743	0.1325	3.2250
6	0.5 mol I_2 + 0.5 mol I_4	1,337.0	0.0311	0.1430	3.1833
7	0.5 mol I_2 + 0.5 mol I_5	1,224.9	0.1283	0.2474	4.4416
8	0.5 mol I_3 + 0.5 mol I_4	1,205.1	0.0412	0.0946	2.8031
9	0.5 mol I_3 + 0.5 mol I_5	1,113.3	0.1789	0.1990	4.0614
10	0.5 mol I_4 + 0.5 mol I_5	1,183.7	0.0663	0.2094	4.0197

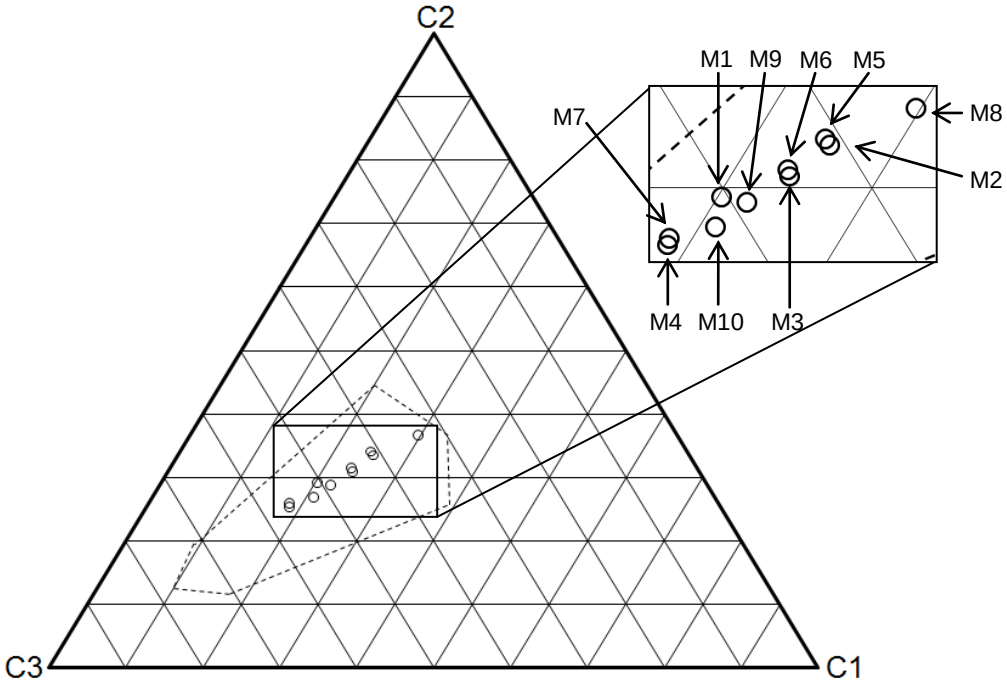

Figure 2: Ternary diagram representing IL binary mixture design results

5. Conclusions

A systematic visual approach to design binary mixture of ILs as CO_2 capturing solvent is proposed in this work. This approach is developed based on property clustering technique and GC methods to predict properties of IL mixtures. The significance of this approach is that IL mixture design problems, which can be described by three or more properties, are analysed visually on a ternary diagram and provide useful insights to user. An illustrative case study is solved to demonstrate the proposed approach. Ten possible IL binary mixtures are determined as possible CO_2 capturing solvents, from five lately tested pure ILs. In future, economic and environmental aspects can be included for screening and evaluation purpose.

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