

DELA NOVEL MODEL FOR SUSTAINABLE SYSTEM DESIGN: A REVIEW OF RELATED CONCEPTS AND INSIGHT ON POTENTIALS OF IONIC LIQUIDS SOLVENTS

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ABSTRACT

Green Chemistry and Life Cycle Design are some of the approaches being used to reduce environmental pollution. Whereas, Green chemistry utilizes a set of principles that reduces or eliminate the use/generation of hazardous substances in all steps of particular synthesis or process, Life Cycle Design is aimed at reducing aggregate

environmental impacts associated with product systems by integrating both product and process design. Unfortunately, the application of either Green chemistry or Life Cycle Design does not make a system wholly sustainable. A sustainable system requires that all the three pillars (i.e., social, economic, & environmental) of sustainability be applied for product and process design. Accordingly, this study proposes an integrated green chemistry and life cycle DELA model for sustainable system design. The model addresses the limitations of the two concepts with an insight on ionic liquids solvent by synchronizing green chemistry with Life Cycle Design and further integrating them with sustainability.

KEYWORDS: Green Chemistry, Ionic Liquids, Sustainability, Life Cycle Design

1. INTRODUCTION

Sustainability is based on a simple principle: Everything that we need for our survival and well-being depends, either directly or indirectly, on our natural environment. It creates and maintains the conditions under which humans and nature can exist in productive harmony that permit fulfilling the social, economic and environmental requirements of present and

future generations. The concept got its root from understanding the need to create equilibrium in systems, thereby minimising and/or avoiding waste (Simon, 2008).

Sustainable chemistry is defined as the implementation of the concept of sustainability in the production and use of chemicals and chemical products and the application of chemistry and chemical products to enable sustainable development (Bahri et al, 2016). There exist two possibilities for addressing sustainability. The green chemistry concept which is based on a set of 12 principles that are aimed at reducing energy usage and waste materials; and producing or utilising safer products and processes. Life cycle design (LCD), aimed at integrating both product and process design in a single function to more effectively reduce aggregate environmental impacts associated with product system. It focusses on the extension life (i.e. durability, adaptability, reuse and recyclability/remanufacture) which is atop its strategies (Christopher, 2017). Life Cycle Design is linked to sustainability through the conventional development phases of a product and its design options: the *holistic* LCD approach is where all possible factors are considered in product design, whereas the *non-holistic* LCD approach is where a single factor or a combination of factors that are non-exhaustive are considered in the design of a product. In addition, the *strategic* approach is where factors of interest considered more critical or advantageous in achieving the set objectives/goals of the LCD are prioritised. Another approach is the *ad-hoc* approach which reviews an existing design that has most probably been deployed, up and running, in order to correct undesired effects of the products life cycle on the environment. The classical approach however, involves the use of precise, standardised and advanced decision-making tools in conducting the Life Cycle Assessment (LCA) (Christopher, 2017).

Although green chemistry and the LCD have been identified as sustainability tools, the application of any one of the two does not guarantee a sustainable system. The concepts dwell more in addressing improvements in eco-efficiency than in addressing the whole pillars of sustainability which will ultimately guarantee a holistic sustainable system developed in this paper (James Clark, 1999, Anastas and Eghbali, 2010).

2.0 Literature/Theoretical underpinning

2.1 Environmental Sustainability

Sustainable development has its roots in ideas about sustainable forest management which were developed in Europe during the seventeenth and eighteenth centuries (Am, Al-kouri, 2013). In response to a growing awareness of the depletion of timber resources in England,

John Evelyn argued that "sowing and planting of trees had to be regarded as a national duty of every landowner, in order to stop the destructive over-exploitation of natural resources" in his 1662 essay *Sylva*. In 1713 Hans Carl von Carlowitz, developed the concept of managing forests for sustained yield. His work influenced others, including Alexander von Humboldt and Georg Ludwig Hartig, leading in turn to the development of a science of forestry. This, in turn, influenced people like Gifford Pinchot, first head of the US Forest Service, whose approach to forest management was driven by the idea of wise use of resources, and Aldo Leopold whose land ethic was influential in the development of the environmental movement in the 1960s. However, environmental sustainability as a concept only came into prominence in 1987 following the report of the World Commission on Environment and Development where it was defined as development that meets the needs of the present without compromising the ability of future generations to meet their own needs. Several other definitions were subsequently proposed, amongst them is the definition by XXX; as the practice of maintaining processes of productivity indefinitely natural or human made by replacing resources used with resources of equal or greater value without degrading or endangering natural biotic systems (JA DU et al, 2006).

The emergence of sustainability therefore, is as a result of significant concerns about the unintended social, environmental, and economic consequences of rapid population growth, economic growth and consumption of our natural resources. Barton and Du Plessis maintains that in order to achieve sustainability, there must exist a reasonable level of balance of interactions among the social economic and environmental sectors (Alley and Leak, 2004).

Accordingly, Social sustainability, Environmental sustainability, and Economic sustainability are thus identified as the three pillars of sustainability (fig) whose principle is guided by the provision of Barton and Du Plessis: ...that for the complete sustainability problem to be solved all three pillars of sustainability must be sustainable (Purvis, 2019). Of the three pillars, the most important is environmental sustainability (Pardeep, et al, 2021). If this is not solved, then no matter how hard we try the other pillars cannot be made strong because they are dependent on the greater system they live within the environment (Basiago, 1999).

Herman Daly therefore defined Environmental Sustainability as the rate of renewable resource harvest, pollution creation, and non-renewable resource depletion that can be contained indefinitely (Mensah, 2019); he further posited as follows: for renewable resources, the rate of harvest should not exceed the rate of regeneration (sustainable yield) for pollution,

the rate of waste generation should not exceed the assimilative capacity (sustainable waste management) for non-renewable resources, their depletion should require comparable development of renewable substitutes.

Thus, environmental sustainability concerns the natural environment and how it endures and remains productive and diverse. Since natural resources are derived from the environment, the state of air, water, and the climate are of particular concern (purvis, 2019). In consideration to this, climate change was first identified as an issue of international concern in 1979 at the first world climate conference. Various other conferences aimed at addressing the causes and impacts of climate change followed (Pardeep, 2021).

The first IPCC assessment report released in 1990 led to governments addressing the need for sustainability and negotiating global treaty on climate change in earnest (IPCC, 2019). The IPCC Fifth Assessment Report outlines current knowledge about scientific, technical and socio-economic information concerning climate change, and lists options for adaptation and mitigation. The Kyoto protocol in 1997, which became effective in 2005, was the major international agreements linked with the United Nations Framework on Climate Change (UNFCCC). In one of its principles under article 3 of the convention, the right to promote sustainable development was recognised. It recognises that addressing climate change should not be at the expense of sustainable development but that action should be integrated into development programs in ways that are appropriate to domestic circumstances; thus the share of emissions originating in developing countries will grow to meet social and development needs (IPCC, 2019). The 2005 World Summit on Social Development identified sustainable development goals as economic development, social development and environmental protection. This view has been expressed as an illustration using three overlapping ellipses indicating that the three pillars of sustainability are not mutually exclusive and can be mutually reinforcing. After similar other conferences along the years, parties to the UNFCCC reached a landmark agreement in Paris on 12 December 2015. The new treaty ends the strict differentiation between developed and developing countries to put forward their best efforts to strengthen them in the years ahead. This include for the first time requirements that all parties report regularly on their emissions and implementation efforts and undergo international review (IPCC, 2019).

It should be noted here that in addition to establishing climate change and the efforts being put to its mitigation, a dual relationship between sustainable development and climate

change has been identified (IPCC, 2019). On the one hand, climate change influences key natural and human living conditions and thereby the basis for social and economic development, while on the other hand, society's priorities on sustainable development influence both the greenhouse gas (GHG) emissions that causes climate change and vulnerability. Environmental sustainability requires society to design activities to meet human needs while preserving the life support systems of the planet. This, for example, entails using water sustainably, utilizing renewable energy, and sustainable material supplies (e.g. harvesting wood from forests at a rate that maintains the biomass and biodiversity) (IPCC, 2019).

2.2.Green Chemistry

Green chemistry is a trans-disciplinary field encompassing all facets of chemistry, engineering, biology, toxicology and environmental science (Anastas, and Eghbali, 2010). While green chemistry is regarded as a chemical philosophy, it does apply to environmental sustainability. Green chemistry, a term coined in 1991 by Paul T. Anastas is guided by a set of principles that encourage the creation of safer, more efficient, and more sustainable designs for chemical products, feed stocks, and processes. The application of green chemistry in the industries, is believed to eliminate the use or generation of hazardous substances in the design, manufacture and application of chemical processes. Below are the twelve principles of green chemistry:

1. Prevention; It is better to prevent waste than to treat or clean up waste after it is formed.
2. Atom economy; Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Less hazardous chemical synthesis; Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Designing safer chemicals; Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. Safer solvents and auxiliaries; The use of auxiliary substances (e.g. solvents, separation agents) should be made unnecessary whenever possible and innocuous when used.
6. Design for energy efficiency; Energy requirements should be recognized for their environmental and economic impacts and should be minimized.
7. Use of renewable raw materials; A raw material or feedstock should be renewable rather than depleting, wherever technically and economically practicable.

8. Reduce derivative; Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalysts; Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Design for degradation; Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Real-time analysis for pollution prevention; Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Inherently safer chemistry for accident prevention; Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires.

2.2.1 Green Chemistry and Environmental Sustainability

Following the above review, it will be noted that the terms - environmental sustainability and —green chemistry are mutually inclusive. While environmental sustainability is defined as the rate of renewable resource harvest, pollution creation and non-renewable resource depletion that can be sustained indefinitely; it can only be achieved through the design of chemical products and processes that reduces or eliminate the use and generation of hazardous substances. Green chemistry through the application of its principles is a tool used in addressing these (Anastas and Eghbali, 2010).

There are a number of review articles that discuss aspects of green chemistry and sustainability of the different reviews, the solvent and sustainable chemistry review done by Welton T. emerged as one of the most comprehensive reviews which linked green chemistry and sustainability (James Clark, 1999). The review identified that the green nature of solvents do not make them sustainable. The author comment thus; the appropriate selection of an established solvent for a process can greatly improve the sustainability of a chemical process; the sustainability of a chemical product or process is necessarily the result of a complex interaction of environmental, technological and economic factors (which can be predicted through techno-economic modelling such as the life cycle assessment LCA). In the author's conclusion, the implementation of the concept of sustainability in the production and use of

chemicals and chemical products require that chemicals processing must be both environmentally and commercially sustainable (Alley and Leaks, 2004).

The use of renewable feed stocks in industry as an application of green chemistry has been discussed elsewhere. In their review Ferran A. et al, discussed extensively on the use of carbohydrate feedstock for sustainable process and products; and the role of green solvents in manufacturing of industrial carbohydrate-based products. The authors succeeded in the use of fructose as the starting material for preparation of new class of ILs. The ILs exhibit tunable solvent properties much like the conventional imidazole based ILs and have been applied as recyclable solvents for the Heck reaction of aryl iodides. Another outstanding success recorded is the use of ILs as soluble functional support for the synthesis of trisaccharide. The approach provided a simplified purification that does not require chromatography during synthesis and also offered the advantages of solution phase synthesis (Christian and Thomas, 2011).

Green chemistry addresses the efficient utilisation of renewable raw materials, eliminates waste and avoid the use of toxic and or hazardous solvents and reagents in both product and process in order to achieve sustainability. Green chemistry is thus one of the powerful tools to use on the path to sustainability (Sheldon, 2014).

2.3. Green Solvents

Until in the recent years when solvent free reaction in some processes became a possibility, solvents have always been used in most chemical processes. Solvents are being used as reaction media for separation, influencing reaction rate and selectivity, dissolution of solids, heat management and extraction (Jessop, 2011). The toxicity and volatility of many of these organic solvents such as toluene, xylene, benzene, methanol and ethanol posed serious threats to the environment. As a result of their industrial application, about 20 million tons per year of volatile organic compounds are discharged into the atmosphere (Lewandoski, 2014). Studies on occupational and environmental exposures lead to establishing their effects to both human and the environment. Direct consumption, inhalation, adsorption and ingestion of the toxins through contaminated soil, water or air are some of the mechanisms of exposure that lead to cancer, dermatological and neurological issues in humans (Nikita, et al, 2016). This gave birth to the interest for the development of safer reaction mechanisms and the synthesis of safer chemicals that are today termed green solvents. Green solvents are derived from biomass e.g. lactate esters, super critical carbon dioxide and ionic liquids (ILs) (Caibo

Yue et al,2011). The subject of greener alternative solvents has been specifically addressed in principles 3, 4 and 5 of the 12 principles of green chemistry. It provides for the design of safer chemicals and products that will be fully effective yet have little or no toxicity (Zakwrzweska, et al, 2011).

Green solvents are characterised by low miscibility in water, low toxicity, low volatility, recyclability and easily biodegradable (Nilson et al, 2002). In fact, replacing a —non- green solvent with a green solvent will improve a process' environmental performance. As a result of the need in replacing non-green solvents with green solvents, different solvent selection guides were developed (Wanessa, et al, 2012). In his review, Welton T (2015) compared four main solvent selection guides developed by SmithKline Beecham, Pfizer 'traffic light', Sanofi and Innovative Medicines Initiative (IMI)-Chem21. Although, some general agreement between the guides were observed, it is concluded that the green solvent guides do not consider the use the solvent will be put to. The agreement observed between the guides are those regarding occupational health and safety, toxicity, volatility and recyclability among others. Hence, the various greensolvents categorisation based on impacts (SmithKline Beecham guide), based on desirability (Pfizer 'traffic light' guide), based on chemical group (Sanofi guide) and based on hazard (Innovative Medicines Initiative (IMI)-Chem21 guide) (Imperato et al, 2012). For the purpose of this study the pfizer selection guide is considered one that is able to make a general categorisation. The Pfizer green solvent selection guide classified the solvents into three classes; preferred, usable and undesirable, ILs green solvents falls within the class of preferred solvent. This is premised on the fact that ILs have extremely low vapour pressure and high thermal stability, thus offering advantages such as product recovery, ease of containment and recycling ability (Kokorin, 2011).

2.3.1. Ionic Liquids (ILs) as Green Solvents

Ionic liquids are a class of non-molecular ionic solvents with low melting points (<100°C) and negligible vapour pressure usually consisting of an organic cation and polyatomic inorganic anion (Wu, Ling and Zhang, 2009).

The first report of an IL (ethylammonium nitrate), goes back to a century but could not be applied widely due to its unstable nature. Sequel to this, scientists achieved the synthesis of ILs with unique physicochemical properties in the 1990s (Figoli et al, 2014). The ILs known as the first generation ILs exhibit unique properties such as chemical and thermal stability, negligible vapour pressure, high polarity, low melting points and high ionic conductivity. The

second generation ILs, are tunable, thermally stable and can dissolve many compounds without volatility. Nowadays, third-generation ILs are being designed with the main goal of achieving specific biological properties, such as enzymatic stability (Medina and Camy, 2014).

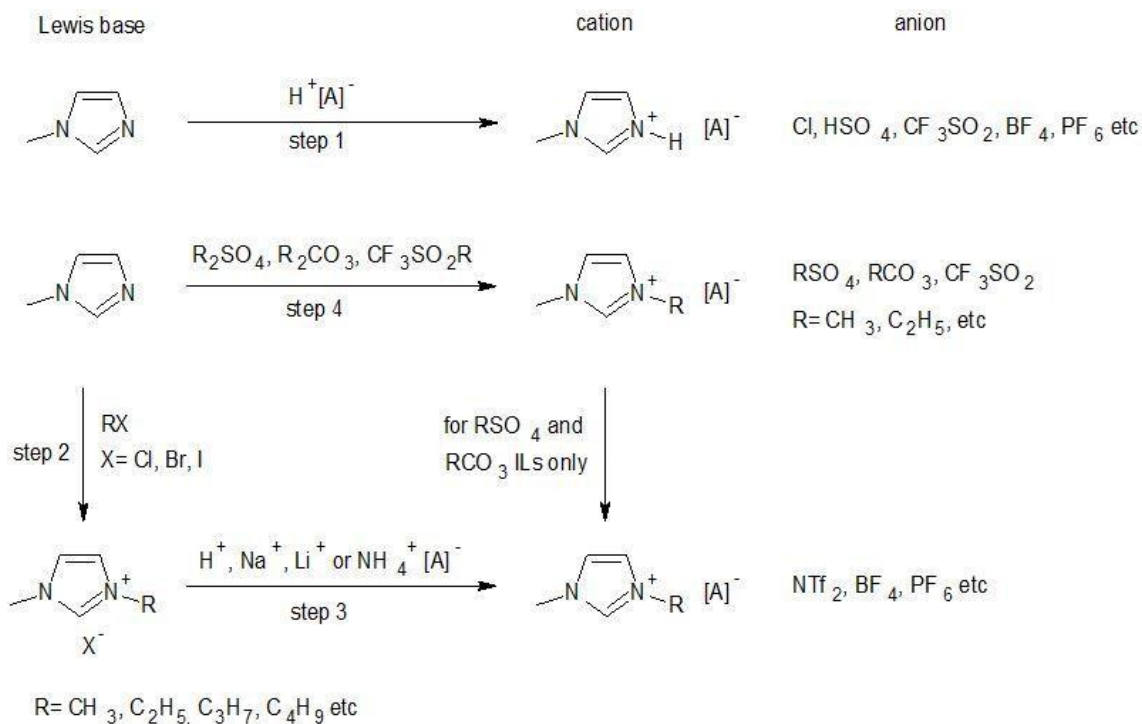


Fig. 1: Ionic Liquids Syntheses Routes.

http://www.intechopen.com/source/html/40049/media/image3_w.jpg

2.3.2 Ionic liquids structure

Earlier research on ILs structure; bromide mono-hydrate anions ($[C_{12}MIM][Br \cdot H_2O]$ and $[C_{14}MIM][Br \cdot H_2O]$) revealed the planar nature of the imidazolium head groups, the presence of a water molecule and the bromide anion at the hydrophilic (imidazolium head groups) parts and the formation of a bi-layer due to the cation alternating (A. Getsis) (Enres and Abidin, 2006). The imidazolium head groups are held together by electrostatic interactions with bromide anions and water. The water hydrogen-bromide distances are in the range for water hydrogen-bromide hydrogen bond (225-226 pm). It is thus presumed that the alternating nature of the cation will not be unconnected with the polymeric nature of ILs reported elsewhere (Datta and Henry, 2006).

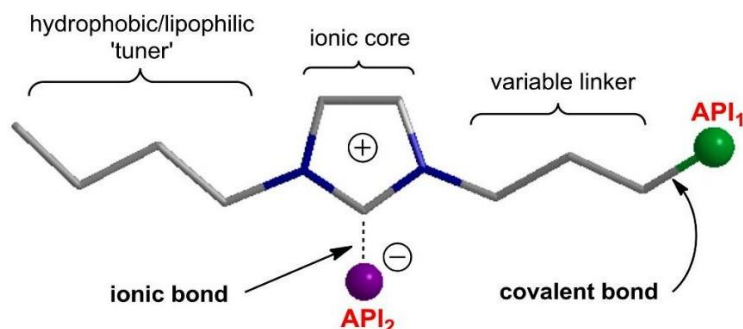


Fig. 2: Structure of imidazolium based ionic liquid explaining various types of interactions source: <http://cdn.phys.org/newman/gfx/news/hires/2015/ionicandcova.jpg>

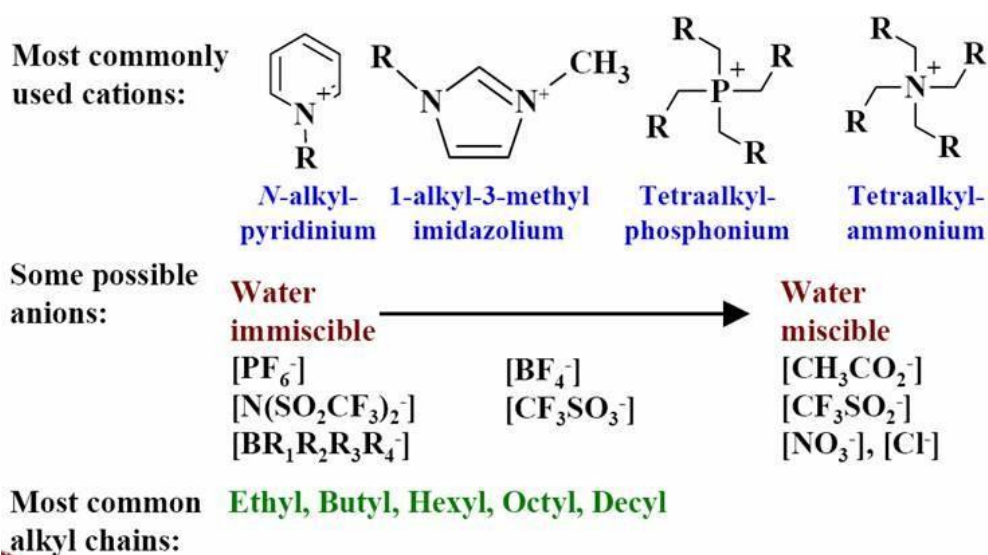


Fig. 3: http://lem.ch.unito.it/didattica/infochimica/Liquidioni/Liquidioni_File/Composition.jpg

In general, ILs properties are a function of either cation or anion; e.g. the density and viscosity are more of cationic effect, while melting point is more of anionic effect (Sungji et al, 2009).

Studies on the effect of water on the structure of ILs have revealed that water can act as a co-solvent with ILs to dissolve substances that would otherwise not be soluble in the ILs. It concluded that the formation of H-bonding between water and anions in ILs may have several other implications. Firstly, it demonstrates that the origin of water absorption from the air in some ILs arises from the water interaction with anions. The presence of water in ILs may have important implications on the properties of ILs, such as conductivity, viscosity and diffusivity. The water content in ILs is also a direct correlation with the strength of H-bonding between the water and anions. In addition, the molecular state of H-bonded water

molecules may affect the reactivity of some solutes dissolved in ILs (Garay et al, 2007).

2.3.4 Solvation and polarity of ionic liquids

Solvation and polarity of solvents explains the interaction between solvent molecules & solutes and the possibility of such interaction (Pereira et al, 2011).

By IUPAC definition, solvation is an interaction of a solute with the solvent, which leads to stabilization of the solute species in the solution. It involves different types of intermolecular interactions: hydrogen bonding, ion-dipole and dipole-dipole attractions of van der Waals forces. The hydrogen bonding, ion-dipole and dipole-dipole interactions occur in polar solvents. Ion-ion interactions occur in ionic solvents (Tom Welton, 2015).

One way of reporting solute-solvent interaction is assessing the reduction and/or decrease of solute concentration in solvents otherwise known as infinite dilution coefficient. An appropriate parameter that can be used to describe solute-solvent interactions at infinite dilution coefficient is 'solvation' (Medina and Camy, 2014).

A number of studies on the solvation nature of ILs exist. Shim et. in their studies concluded that cation influences solvation. Moreover, Kobrak et. al observed the solvation of a chromophore using time resolved fluorescence spectroscopy and concluded that collective contribution of both the cation and anion is responsible for solvation in ILs and that the different time-scales observed in imidazolium ILs may represent different lengthscales for solvent response (Prat, Hayler and Wells, 2014).

Polarity is another important property of solvents. The IUPAC definition of solvent polarity is the sum of all possible specific and non-specific intermolecular interactions between the solvent and any potential solute (Capello et al, 2007). An extensive study of this property for ILs was done by Poole C.F using the E^N scale of solvent polarity.

Different measurement techniques have been used in quantifying solvent polarity. Accordingly, studies have shown that ILs are polar and that the polarity of tetraalkylammonium salts and 1,3-dialkylimidazolium salts are similar to dimethylsulfoxide at the low side while at the top side they are similar to the polarity of formamide and aliphatic alcohols. A small increase in polarity of tetraalkylammonium salts was observed when the alkyl chain increases unlike in the case of 1,3-dialkylimidazolium salts. In the latter the introduction of a polar functional group such as hydroxyl showed a significant increase in

polarity and an opposite situation when methyl group is introduced at C-2 of IL imidazolium cation (figure 4), indicating that the ET(30) is a function of the hydrogen bond acidity. In general, the solvent strength of ILs revealed that ILs exhibit solvent strength greater than most polar aprotic solvent (acetonitrile) (Rogers et al, 2005).

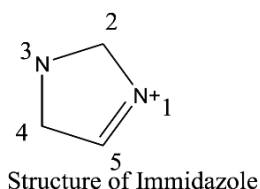


Fig. 4: Structure of imidazole. Adapted from <https://www.sciencedirect.com>.

2.3.5 vapor pressure

Various studies have established the negligible vapour pressures ($\approx 10^{-10}$ Pa at 25°C), of ILs. Hence the ability to distill some ionic liquids under vacuum conditions at temperatures near 300°C and the possibility to use ILs as replacement to volatile organic solvents. This extraordinary property has also made them recoverable for re-use and contributed to the classification of ILs as green solvents (Michael et al, 2013).

The low vapour pressures of ILs were measured in various studies; Zaitsau DH, et al, measured the vapour pressures of various ILs by the integral effusion Knudsen method. Thermodynamic parameters of vaporization for ILs were calculated from these data. The absence of decomposition of ILs during the vaporization process was proved by IR spectroscopy. Enthalpies of vaporization of ILs were correlated with molar volumes and surface tensions of the compounds. Bier M, and Dietrich S. in their work, attributed the phenomenon of ILs low vapour pressure to a combination of both strong ionic character and low melting temperatures below 100°C . The authors compared the distillation of ILs and non-ionic liquids, as such concluded that the even stronger ionic character of inorganic fused salts would in principle lead to even lower vapor pressures; however, these cannot be reached for their liquid state because they are preempted by a significantly higher freezing and thus triple point temperature (AL-Garay and James, 2007).

2.3.6 Tunability

Ionic liquids are considered designer solvents due to the possibility of manipulating their characteristics (e.g. polar/less polar and hydrophilic/hydrophobic) by combining the right anions and cations to meet the desired property for a specific application [S. P. M. Ventura et

al.). The solvent properties of ILs is a function of H-bond donor /acceptorability of salt while physical properties of ILs affected by charge distribution on the anions, H-bonding, and polarity etc.

In their work, S. P. M. Ventura et al. designed hydrophobic ILs of low ecotoxicity by the manipulation of their chemical structures. Their work was premised on the fact that not all hydrophobic ILs can be exempted from being toxic. The impact therefore of aromaticity on the toxicity of different cations (pyridinium, piperidinium, pyrrolidinium and imidazolium) and hydrophobic anions (bis(trifluoromethylsulfonyl)imide [NTf₂] and hexafluorophosphate [PF₆]) was analysed. It concluded that If the potential of this “designer solvent” character is fully understood and applied, the full potential of ILs may be released with solvents not only with enhanced performances, but also with a lower environmental impact and a greener character. (Xianzhao et al, 2018).

Knowledge on both the anionic and cationic effect of ILs allowed also for the designing of task specific and biodegradable ILs (Earlie et al, 2006). Task-specific ionic liquids (TSILs) contains functional groups that is covalently tethered to the cation or anion (or both) of the ILs. Accordingly, incorporating a catalytic active group on the cation or anion, a new type of ionic liquid catalytic material could be obtained, therefore allowing for a specific application. Robin D. Rogers et al. were among many authors that published on TSILs; one of their work was on the application of TSILs for the selective liquid/liquid extraction of heavy metals from aqueous systems. Functionalized imidazolium cations with thioether, urea, or thiourea derivatized side chains act as metal ligating moieties, whereas the PF₆⁻ anions provide the desired water immiscibility (Figure 1). Nernst distribution ratios were reported for Cd²⁺ and Hg²⁺ to be ≤ 380 (Rogers et al, 2007).

Furthermore, Chaturvedi Devdutt et al. reviewed the reaction selectivity of TSILs in organic synthesis. The review offered an update on recent developments in the field of TSILs with an emphasis on their applications in synthetic organic chemistry (Mai, Ahn & Koo, 2014). The work of Salunkhe and their coworkers wherein the best yields of the acylated products were achieved using 1-methoxyethyl-3-methylimidazolium methane sulfonate [MOEMIM]OMs as a TSIL, was among the many studies reviewed. The investigation illustrated the benefits of solubility and recoverability, as well as efficient reaction conditions, which ionic liquids can provide for nucleosides (Plechova and Seddon, 2008).

Biodegradability on the other hand, has been achieved due to the ability of tuning ILs to the desired property. It is one of the properties that qualifies and/or improve the non-toxicity of ILs (Wang, et al, 2007). Several studies have been accomplished in this respect and due to these studies, some ILs that are non-biodegradable are found to exhibit a certain level of toxicity (Greaves & Drummond, 2008). The first reported investigation on this, is the work of Jastorff and co-workers. Therein, an account of the risk associated with ILs toxicity based on five ecotoxicological indicators (release, spatiotemporal range, bioaccumulation, biological activity and uncertainty), which allow a direct comparison with common organic solvents was taken. This subsequently led to the design and synthesis of biodegradable ILs (Tokuda, et al, 2006).

The design of biodegradable ILs, is a function of the ability to tune in the anionic/cationic property of the IL to the desired need. Accordingly, Garcia M. Teresa et al. designed, prepared and evaluate biodegradable ILs containing ester or amide groups in the alkyl side chain. The group established that the introduction of a group susceptible to enzymatic hydrolysis greatly improves the biodegradation (OECD 301D_Closed Bottle Test) compared with the commonly used dialkylimidazolium ILs, bmimBF₄ and bmimPF₆. For the 3-methyl-1-(alkyloxycarbonylmethyl) imidazolium bromide series, the greatest biodegradation was observed when alkyl = butyl, pentyl, hexyl and octyl. Thus, conclude that the corresponding amide analogs proved to be poorly biodegradable. In a different study, the group established that ILs biodegradability is more influenced by the anion. Similarly, Shaohua Gou, et al. investigates various types of ILs based on polyethyl glycol and applied them for the inhibition of shale hydration. All the polyethylene glycol with molecular weight 200- based ILs showed biodegradability (Anderson, et al, 2002).

Consequent upon these, the most important parameters in the design of biodegradable ILs were summarised to include a) the presence of potential sites of enzymatic hydrolysis (e.g. esters and amides), b) the introduction of oxygen in the form of hydroxyl, aldehyde or carboxylic acid groups, c) the presence of unsubstituted linear alkyl chains (more than four carbons) and phenyl rings, possible sites of attack by oxygenases (Fletcher, 2003).

2.3.7 Recyclability

This property of ILs has made them more attractive for various applications owing to their cost, waste generation and accumulation of impurities arising from various applications (IUPAC, 2006).

Accordingly, Wu B. et al. reviewed the studies carried on the existence form (ions, ion pairs, or supra molecule) of ILs which consequently allow for their recycling (Calvio et al, 2010).

Similarly, Koo Yoon-Mo and co-workers, presented a comprehensive summary on the methods used for recovery and recycling of ILs. Therein, the authors reviewed methods such as distillation, extraction, adsorption, induced phase separation, membrane based methods e.t.c. Methods used for ILs recycling, have been established to be dependent on the ILs properties. Thus, for low vapour pressure ILs, distillation of volatile solvents is a preferred technique in the recovery and recycling of the ILs. However, for the separation of non-volatile and thermally-sensitive solutes, methods such as extraction with organic solvents or supercritical carbon dioxide and membrane separation processes are best applied (Zhang et al, 2008). Decantation can easily be used for the recovery and recycling of hydrophobic ILs. They are immiscible and make separated phases with water easy. Although distillation of hydrophilic ILs from its diluted aqueous solution can be used in the recovery of hydrophilic ILs, it consumes a high amount of energy. Thus, induced-phase separation by adding salts (salting-out process), supercritical carbon dioxide, or changing temperature; adsorption and membrane-based methods have been investigated. Furthermore, micellar based ILs can be separated by membrane-based methods (e.g. filtration) or force field separation (e.g. centrifugation) (Lomba, et al, 2011).

Owing to these properties, the concept of sustainability can be achieved with solvents like ILs. Sustainable chemicals improved management of environmental, social and economic impacts that are as a result of business activity while seeking a balance (Chen and Wang, 2008). In order to strike a balance, there is however the need for a holistic sustainable system wherein both the product and the process are sustainable. A system in which to achieve sustainability is linking of green chemistry with the life cycle approach.

2.4 Life Cycle Approach

Most studies on ILs have focused mainly on the green nature of ILs and their applications. According to Welton T. (2015), the selection of solvent for a reaction can dramatically affect the reaction outcome. Hence, it is possible that a replacement of a 'non-green' solvent by a 'green' solvent could lead, for example to a lower yield of the product and greater waste, or need for harsher operating conditions that require more energy. In these cases, the process can become less environmentally sustainable overall. In order to thoroughly understand how a solvent change can affect the sustainability of a process, it is necessary to understand all its

impact on the overall process. Hence the Idea that a liquid can be regarded as inherently green' is somewhat naive, even irrelevant. What matters is whether the use of one solvent or solvent system rather than another can give a more sustainable process and/or product –(Tao, et al, 2005). The emergence of sustainability has made it clear that the green nature of a product/process is not capable of addressing sustainability in a holistic manner. One of the major barriers of green chemistry, is the lack of comprehensive evidence of good environmental and economic performance of proposed green chemical processes (Lapkin et al. 2004). The life cycle approach is another concept that contributes to addressing the sustainability question.

The Life Cycle Assessment (LCA) is an environmental sustainability tool that provide a quantitative assessment of the environmental impact of a product over the entire life cycle. It is used to evaluate the environmental impacts –from cradle to grave of a target product/chemical (Zang, et al, 2008). Bakshi Bhavik R. and co-workers, carried out an LCA study of an IL [BMIM][BF₄] use as a solvent for the manufacture of cyclohexane and in a Diels-Alder reaction. These uses are compared with more conventional synthesis methods (Eckert, et al, 2008). Results indicate that processes that use IL are highly likely to have a larger life cycle environmental impact than more conventional methods. The group concluded that because there are many ILs, with many applications, the few example used are not enough to reach any general conclusions about the greenness of all ILs. However, the life cycle data and approach of the study can be used for evaluating the greenness of more kinds of solvents, processes, and emerging technologies. We have discussed elsewhere the importance of LCA as a tool in product Life Cycle Design (LCD) (Levet, et al, 2013).

The life cycle framework has been associated with environmental assessment than design [Gregory]. The principle of life cycle design originates from concurrent design programs. Unlike its evaluation tool (LCA), the LCD seeks to integrate product and process design in a single function to more effectively reduce aggregate environmental impacts associated with product system (Marinella, et al, 2010). It applies sustainable development principles in evaluating the totality of product effects from raw materials extraction through the various production processes to the consumption and eventual disposal of all possible waste and their impacts to the environment (Kamio et al, 2006). One of the strategies of LCD is the design for recyclability, aimed at closing the material life cycle loop. Furthermore, the life extension strategy of the LCD, focuses on any one or all of these properties; durability, adaptability,

reuse and manufacture. Thus, in developing sustainability through the LCD, five main approaches that are dependent of the design objective have been proposed. The approaches explained in the introductory part of this paper include: i) Non-holistic, (ii) holistic, (iii), strategic, (iv) ad-hoc and (v) classic (Takahiro, et al, 2008).

Arising from the foregoing it is evident that no one individual concept, either green chemistry or LCD can provide a holistic sustainable system. Thus, it is proposed herein, a model that addresses this gap. The solution to this, is the main aim of this study (green chemistry and LCD) In order to address sustainability, the incorporation of green chemistry and LCD.

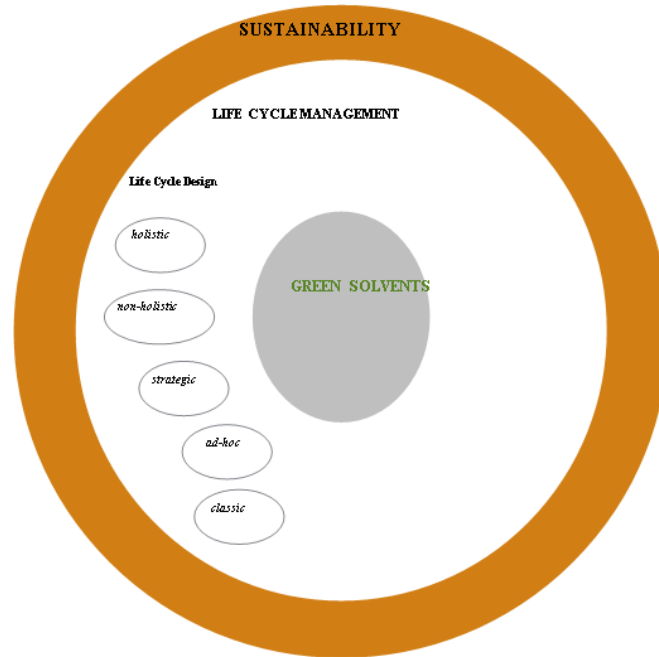
2.5 MODEL FOR THE DESIGN OF SUSTAINABLE IONIC LIQUIDS AND PROCESSES The proposed model is a three staged model that synchronises the concept of green chemistry (specifically on green solvents), life cycle management (the LCD approach) in such a way to consider the multitude of environmental, social and economic in system design.

The *green solvents* layer's primary focus, is on the solvents' design based on the principle of green chemistry. This is taken as the prerequisite to the whole issue of solvents' sustainability, thus chosen as the first layer.

The stage provides that ILs designed, should exhibit green properties such as less/nontoxic, biodegradable, low vapour pressure and recyclability. An appropriate green metric as discussed elsewhere in this paper can be applied to ascertain the greenness of a product or process.

The second stage of the model is the *Life Cycle Management* layer. It integrates the green nature of ILs and their design objective. A prior knowledge on the intended application of ILs is therefore necessary.

The stage addresses the accomplishment of design of sustainable ILs based on any one of the LCD approaches (e.g. strategic approach). Hence, the synchronisation of the whole life cycle of ILs with their green properties to the intended application. The cost effectiveness, commercial viability and environmental viability of the ILs are all taken into consideration (Craig, et al, 2011).



DELA - Model for Sustainable System Design

Life cycle design tools such as the LCA and LCST (life cycle sustainability assessment tool), are better employed to achieve the requirements of this stage.

The *sustainability* layer of this model, provides for the integration of both the green solvents and LCD layers in such a way as to providing sustainability. This layer suggest that unless both the product (ILs) and process are sustainable, sustainability can't be achieved. It provides the mutual dependence of product and process sustainability to achieve a holistic sustainable system. The stage further provides that the whole system must ensure that the economic pillar of sustainability maintains a healthy balance with the ecosystem. It also suggests the preference of product design from renewable sources that will ultimately guarantee less energy consumption, recycling and or better waste management.

Overall, the stage provides that a sustainable system design should not be to the detriment the society and the living environment. In order therefore to ascertain the sustainability of the whole system, sustainability indicators should be applied.

Although indicators at each individual stage will be used, further application of a sustainable indicator as provided in the literature will give a measure of how sustainable the whole system. A sustainability indicator is an operational representation of an attribute of a system (Al-Khoury, 2013). It can provide crucial guidance for decision making in a variety of ways: 1.) it can translate physical and social knowledge into manageable units of information that

can facilitate the decision-making process, 2.) it can help to measure and calibrate progress towards sustainable development goals, 3.) it can provide an early warning, sounding the alarm in time to prevent economic, social and environmental damage and 4.) it is an important tool to communicate ideas, thoughts values (Christopher, 2017).

CONCLUSION

We have developed a holistic model that considers the relationship between green chemistry, life cycle design and sustainability. The model addresses the challenge of change in external environment and economy, it allows for design for a target (non-holistic, holistic, strategic, ad-hoc or classic) purpose.

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