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Review

Methods for recovery of ionic liquids—A review

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ABSTRACT

Ionic liquids (ILs) have attracted much attention in both academics and industries as promising solvents for a diverse range of applications. However, there were little industrial processes employing ILs as current time due to the economical and efficient use of ILs. The economic efficiency can be improved by recycling and reuse of ILs. In the last few decades, several attempts have been made, by the researchers, for recovery and recycling of ILs. This review is intended to present a comprehensive summary on the methods used for recovery and recycling of ILs.

Contents

1. Introduction

Ionic liquids (ILs), also known as room-temperature ionic liquids (RTILs), are salts that are composed only of ions and have melting point below 100 °C [1–3]. Based on their chemical behavior, ILs are divided in two groups: aprotic and protic ILs. The aprotic ILs are also considered as "classic" or "conventional" ILs since their structures are mainly based on bulky organic cations such as imidazolium or pyridinium and large variety of anions such as Cl^-, Br^-, BF_4^-, PF_6^-, etc. Protic ILs, on the other hand, are generally prepared by neutralization reaction of an organic base and an acid or in the other word through proton transfer from a Bronsted acid to a Bronsted base. Up to date, aprotic ILs have received far greater attention than protic ILs although there has been escalating interest in protic IL in recent years [4,5]. ILs, in general, have attracted much attention

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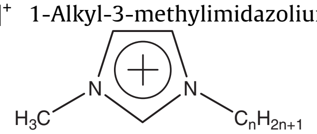
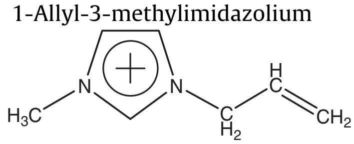
Nomenclature

Abbreviation of ionic liquids

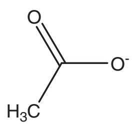
$[C_n mim]^+$ 1-Alkyl-3-methylimidazolium ($n = 1, 2, 4, \ldots$)



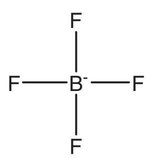
$[Amim]^+$ 1-Allyl-3-methylimidazolium



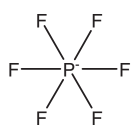
$[OAc]^-$ Acetate



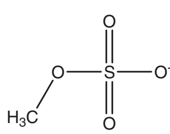
$[BF_4]^-$ Tetrafluoroborate



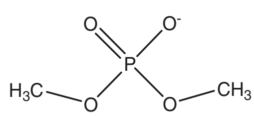
$[PF_6]^-$ Hexafluorophosphate



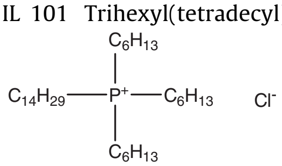
$[MeSO_4]^-$ Methylsulfate



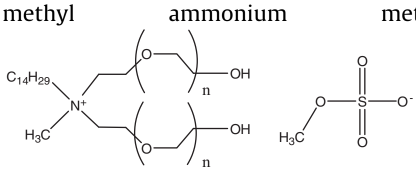
$[DMP]^-$ Dimethylphosphate



CYPHOS IL 101 Trihexyl(tetradecyl)phosphonium chloride



ECOENG500 Cocosalkyl pentaethoxi methyl ammonium methylsulfate



both in academic and industrial communities as a promising alternative for organic volatile solvents due to their unique properties such as negligible vapor pressure, non-flammability, wide electrochemical window, and good chemical and thermal stability [6,7]. They are capable to dissolve huge variety of materials including hydrophobic, hydrophilic and polymeric compounds. In addition, the properties of ILs can be tailored by selecting a proper combination of cations and anions which defined ILs as "designer solvents" [8]. The applications of ILs have been found in a diverse range of fields such as chemical and biological processes, electrochemistry, polymer science and nano-chemistry. In addition, the designable properties of ILs can be used for developing new processes that are technologically, environmentally and economically advantageous [9–16]. However, there was a limited number of industrial processes employing ILs due to their high cost [17]. To resolve the issue of price of ILs an efficient recycling of ILs is crucial for their industrial use, especially for pilot-plant applications. In addition, during industrial application, they might be mixed with other products, which require an efficient separation too. Furthermore, recovery of ILs is also important to resolve the environmental concerns of the disposal, like biodegradation and toxicity [18–23].

Due to low vapor pressure, distillation of volatile solutes is always being the first choice to recover and recycle of ILs. However, for the separation of non-volatile and thermal-sensitive solutes, other methods are applied such as extraction with organic solvents or supercritical carbon dioxide and membrane separation processes. It is important to note that the interaction of ILs with water, which is mainly affected by the size of ILs, hydrophobicity and hydrogen bonding ability of both cations and anions, will determine the techniques used for recovery of ILs. Among the effects, the nature of anions largely determines the behavior of IL-water mixture [24,25]. Hydrophobic ILs which are immiscible and make separated phase with water, therefore they can be easily separated from water by decantation. ILs that are containing both hydrophilic and hydrophobic domains (surfactant-like ILs, e.g. ILs possessing long aliphatic substituents) have tendency to form micelle in water [26,27]. The micellization of ILs depends on the size of these domains (larger the hydrophobic domain, greater the tendency to aggregate) [26]. These aggregated ILs can be separated by membrane based methods (e.g. filtration) or force field separation (e.g. centrifugation). The recovery of hydrophilic ILs, however, is more difficult compared to hydrophobic ILs. For instance, distillation of ILs from its diluted aqueous solutions consumes a high amount of energy and therefore it will make the recovery operation non-feasible. Many methods have been investigated to recover hydrophilic ILs such as the induced phase separation by adding salts (salting-out process), supercritical CO_2, or changing temperature; adsorption; and membrane based methods, etc. Generally, the choice of appropriate separation methods depends on the characteristics of systems/processes. This review is an attempt to highlight and summarize the recent works regarding the methods used for separation and recycling of ILs.

2. Distillation

Distillation is considered as simplest method for removal of the compounds having low boiling point and high thermal stability from ILs (due to their negligible vapor pressure). The volatile compounds can be distilled by vacuum evaporation, column distillation, and molecular distillation. In spite of the fact that energy consumption is high in distillation process, it is usually applied as final step in most of the published studies to recover and recycle of ILs. In these studies, catalysts and products were first removed from ILs media by decantation, filtration, extraction, and washing with water/organic solvents, etc. Contaminated solvents or un-extracted compounds in ILs were further separated by distillation, thus allowing the recycling and reuse of ILs [28–31]. For example, [Amim][Cl] was recovered from aqueous solution of homogenous cellulose acetylation reaction media by molecular distillation. The volatile impurities were distilled as distillate and the IL remained as a residue which was recycled and reused 5 times in the homogenous cellulose acetylation system without any change in the structure [32]. Intersetingly, the ultillizing of microwave heating could enhance the recovery of IL from its aqueous solution in term of operating time and energy efficient [20].