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Toxicity and Biodegradability of Solvents: A Comparative Analysis

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Abstract

Solvents are widely-used in all aspects of chemical sciences. One of the disadvantages of conventional solvents is attributed to the adverse impacts they pose on human health and ecological systems. Emerging class of solvents such as ionic liquids have been proposed to alleviate this problem. In this study, aquatic toxicity and biodegradability of two common industrial solvents are compared to those of two ionic liquids. Results from this study highlight the importance of solvent selection considering the information on the toxicity, biodegradability and fate and transport properties of selected solvents altogether.

Keywords: toxicity; biodegradability; industrial solvents; ionic liquids; freshwater organisms

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1. Introduction

Liquid-liquid extraction processes, which are normally carried out by the means of optimal solvents, are extensively used in petroleum refining as well as petrochemical and chemical industries. In these processes, undesired compounds will be removed from feed by solvents whose solubility are high towards the compounds which should be extracted out of the system, but low towards the components which should remain in the solution.[1-7] In lubricating oil manufacturing facilities, it is conventional to remove aromatic substances from the feed to enhance the desired properties of the final product. Every day, large amounts of industrial solvents are used in different industrial plants,[8-9] this fact furthermore shows that the adverse impacts coming from these chemicals should addressed accordingly.

Sulfolane and furfural are industrial solvents which are widely exploited in industrial plants all over the world,[10-20] These solvents have high selective solubility of aromatic components, therefore can be used for aromatic-aliphatic extraction processes. For these solvents, the higher boiling points make the process of regenerating the process solvent challenging. These solvents are both soluble in water the very fact that makes their presence in water compartments likely.

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In this study, also two organic salts (i.e. Ionic liquids) which also have high solubility of aromatic materials were chosen. These multi-atomic salts can be made to be liquid at room temperature and to have high solubility toward a component of interest. Ionic liquids with low viscosity and melting point are proved to be promising candidates for use in liquid-liquid extraction (LLE) processes.[21-23]

2. Methods

In this study, to evaluate the adverse impacts that industrial solvents may have on the human health and ecosystem, long-term persistent of four solvents are studied based on their biodegradability in the water bodies by the aquatic organisms. Thus, two conventional solvents, sulfolane and furfural, and two non-conventional compounds, 1-butylpyridinium chloride, [BPy] Cl, and 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim] BF_4 ionic liquids were considered in the current endeavor.

3. Results and discussions

The key physical properties of the selected solvents, which affect their long-term impacts on the environment, are listed in Table 1.

Table 1: Physical properties of selected solvents

Solvents	Boiling Point (ºC)	Vapor Pressure @ 25ºC [kPa]	Water solubility @ 25ºC [g/l]
Furfural	162	0.3	83
Sulfolane	285	Negligible	Miscible
[BPy] Cl	>400	Negligible	43.2
[BMIM] BF_4	>400	Negligible	Miscible

From Table 1 it is observable that all the solvents selected for this study have boiling points higher than water (much lower vapor pressures), the very fact that lowers risk of their direct air pollution.

To study the impacts of solvents, toxicity of these compounds towards aquatic organisms: fish, Daphnia Magna and a green algae (PKS) were collected from the literature. These data are tabulated in Table 2.[21, 24-27]

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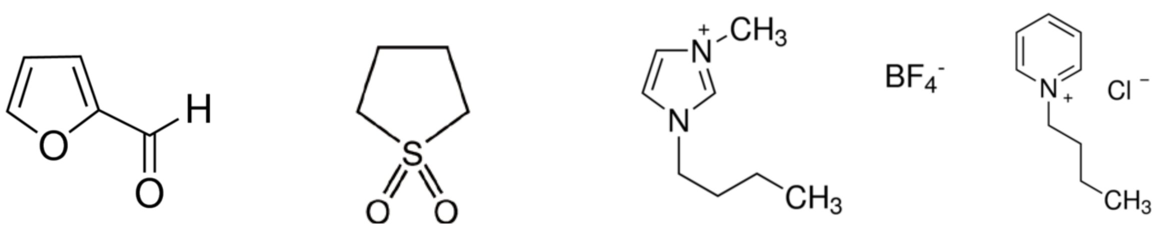
Table 2: Toxicity and bioaccumulation factor of selected solvents

Solvents	LC50 (Fish, fresh water, 96 h) [mg/l]	EC50 (Daphnia, fresh water, 48 h) [mg/l]	EC50: (PKS green algae) [mg/l]	Bioconcentration factor (BCF) [L/kg]
Furfural	10.5	13	45	1.41
Sulfolane	100	852	500	1.3
[BPy] Cl	≥ 100	20	63.9	6.04×10^{-4}
[BMIM] BF_4	≥ 100	10.7	568	8.94×10^{-4}

From Table 2 we can see that in special cases, ionic liquids can be even more toxic than their organic counterparts, which is something that is against the general belief on the greenness of ionic liquids. For instance, [BPy] Cl shows a considerably higher toxicity towards the aquatic microorganism, Daphnia Magna, compared to sulfolane. However, the much lower values of bioaccumulation factors, BCF, for ionic liquids can point towards this fact that their exposure to 'biota' can be significantly lower than organic solvents. In this study, we assumed a similar power of solvency for the selected ionic liquids and the conventional solvents meaning that an equal amount of these solvent is needed for a typical extraction process.

Next, we looked at the chemical structures of the solvents of interest to rationalize their persistent in the ecosystem.

Chemical structures of the selected solvents are shown in Figure 1.



a) b) c) d)

Figure 1: Chemical strcutures of the selected solvents: a) furfural b) sulfolane c) [BMIM] BF_4 d) [BPy] Cl

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As it can be seen from Figure 1, furfural has a more spread out structure with a hydrogen atom relatively loosely connected to the (-C=O) group, so it is easier for aquatic microorganisms (bacteria, algae, etc.) to decompose the solvent and therefore it has a higher rate of biodegradation in water. On the contrary, sulfolane has a more compact structure with two oxygen atoms strongly connected to the 'S' atom making it harder for microorganisms to degrade the compound. For the ionic liquids, case is even worse since the large structure of cations and anions and the strong ionic bonds between the charged particles makes the chance of biodegradation less likely. Table 2 lists the biodegradation rate of the selected solvents.

Table 3: Biodegradability of selected solvents[21,28]

Solvents	**Biodegradability**
Furfural	46% ThOD Readily biodegradable in water 2380 mg L^{-1} d^{-1}
Sulfolane	8 mg L^{-1} d^{-1}
[BPy] Cl	<< 1 mg L^{-1} d^{-1} Not readily biodegradable
[BMIM] BF_4	1.17 mg L^{-1} d^{-1} Slightly Biodegradable

4. Conclusions:

- Although ionic liquids are generally considered as the greener alternative of conventional solvents, due to their negligible volatility, they can be persistent in the freshwater bodies once they are released.

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- Large size of cations and anions in ionic liquids is probably the reason of them not diffusing into the bodies of freshwater organisms, making their bioaccumulation factors meaningfully small.
- Vapor pressure of studied ionic liquids confirms that they mostly have negligible vapor pressure and higher tendency towards being in the liquid phase.

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