Application of deep eutectic solvents (DES) in analytical chemistry

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Abstract: Recent years have been associated with efforts to reduce the impact on the natural environment. A greener approach has been introduced in various areas of science, including analytical chemistry. One of the basic procedures for preparing a sample for analysis is its extraction. Traditional methods involve the use of large amounts of organic compounds, often toxic, with an unfavorable impact on the environment. A representative of the "green" approach to the problem of organic solvents are new materials - deep eutectic solvents (DES). They are promising solvents with many advantages (low toxicity, biodegradability, low cost), which are increasingly used in many chemical and technological processes, including the extraction process.

Keywords: deep eutectic solvents, extraction, green solvents, microextraction

1. Introduction

Sample preparation for chemical analysis is considered to be the most important step in the analytical procedures. During this stage, the sample undergoes many processes and modifications in order to purify, preconcentration, or adapt it to the appropriate analytical equipment. Sample preparation may focus on analyte extraction, matrix transformation, or both. All activities are to ensure a better analytical result [1-2].

Recent years have been associated with paying more attention to "green" analytical techniques, including replacing traditional extraction methods with new, "green" microextraction techniques. This trend in science began with the introduction of green chemistry and its principles. The main goal is to transform the existing analytical techniques in such a way that they would become more environmentally friendly. Most of the assumptions are focused on the elimination of toxic and volatile organic solvents, and reduction of the solvent volume. Another assumption involves the development of direct analytical techniques that do not use chemical reagents [1-4].

There are extraction techniques that do not require the use of toxic solvents, such as static headspace (SHS), or dynamic headspace (DHS), or solid phase microextraction (SPME). However, there are some limitations to these techniques i.e. low sensitivity towards high-boiling compounds, time consumption, and expensive analytical equipment. Green extraction methods include also liquid phase microextraction (LPME) and its modification, i.e. dispersive liquid–liquid microextraction (DLLME), solidification of floating drop dispersive liquid-liquid microextraction (SFD), single drop microextraction (SDME), and hollow fiber-based liquid phase microextraction (HF-LPME) due to the application of very small amounts of solvents. However, these techniques still require the use of small amounts of toxic solvents. Therefore, in recent years, new green solvents that will be more environmentally friendly are searched [1-2, 4-6].

2. Deep eutectic solvents

Recently, deep eutectic solvents (DES) are gaining more and more attention as new generation green solvents. As shown in Figure 1, interest in DES solvents began around 2004, and since then a continuous and intensive increase in publications on this subject has been observed. The use of DES in the extraction process began a little later, in 2012, and a steady increase in research on this subject has been observed since then.

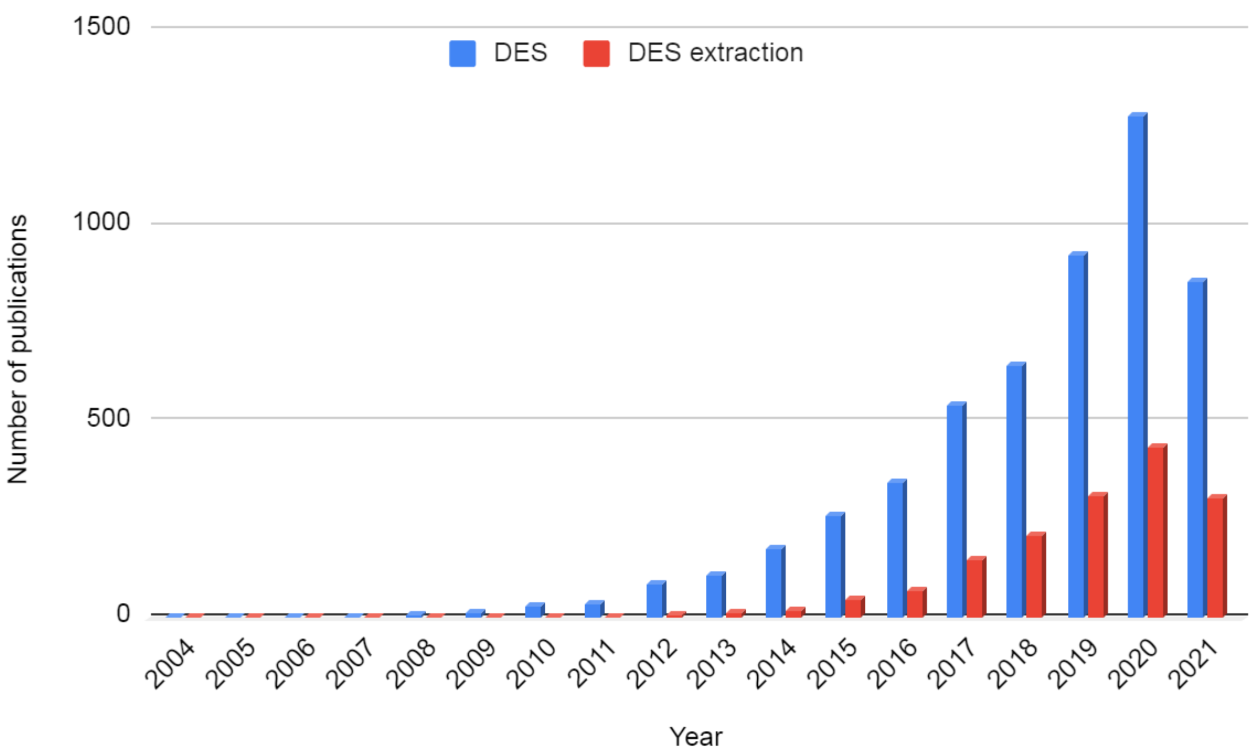

Figure 1: Number of papers published during 2004–2021 on extraction with the DES – based on Scopus database (searched keywords: deep eutectic solvents and deep eutectic solvents extraction; accessed on 24.06.2021).

Deep eutectic solvents are created by mixing two or more components, which can form a new solvent with a melting point much lower than the individual components. The components of DES bind with each other through various interactions, including hydrogen bonding and electrostatic interaction. So, a hydrogen bond donor (HBD) component and a hydrogen bond acceptor (HBA) component can be distinguished. Chemical compounds forming DES are natural, non-toxic, and biodegradable, as a result of which the resulting mixture is also safe for the natural environment. The formation of these solvents is also associated with economic advantages, as the ingredients are inexpensive, and the entire synthesis procedure is simple and cheap and does not require the use of expensive equipment. DES can be hydrophilic or hydrophobic, their nature will be determined by the substrates [7-8].

2.1. DES synthesis

There are two main DES synthesis approaches, including the grinding and heating method. The grinding method involves mixing and grinding two or more ingredients in a mortar with a pestle at room temperature (RT). The great advantage of this method is the lack of formation of unfavorable esters due to the process being carried out at RT. However, this method is very rarely used. The most common heating method is based on mixing two or more components and heating them simultaneously until a homogeneous mixture is obtained. Heating is carried out to about 100 °C. This method is faster and easier, however, it can cause the formation of impurities i.e. hydrogen chloride and corresponding esters if quaternary ammonium salts with chlorine atoms are mixed with carboxylic acids.

Several types of DES can be distinguished. By combining quaternary salts with hydrophilic HAD, the obtained DES will have hydrophilic nature. The use of these DESs has some disadvantages when working with the aquatic environment. Water modifies the connections between the ingredients, and this causes changes in structural properties. As the amount of water in DES increases, the interactions between the components weaken. For this reason, research is conducted mainly on hydrophobic DES, which will remain stable in the aquatic environment [1]. Hydrophobic DES can be obtained by mixing a quaternary salt or terpenes (HBA) with an appropriate HBD compound. Some compounds can be both acceptor and hydrogen bond donors. HBAs based on long-chain ammonium salts are often used in the synthesis of hydrophobic and ionic DES, as the longer hydrocarbon chain enhances the hydrophobic character. In addition in non-ionic hydrophobic DES, components from group of monoterpenes i.e. camphor, eucalyptol can be used as HBA due to their high hydrophobic nature. Long-chain alcohols, acids, amino acids, polyphenols and sugars are often used as HBD [2]. Examples of HBA and HBD are shown in Figure 2.

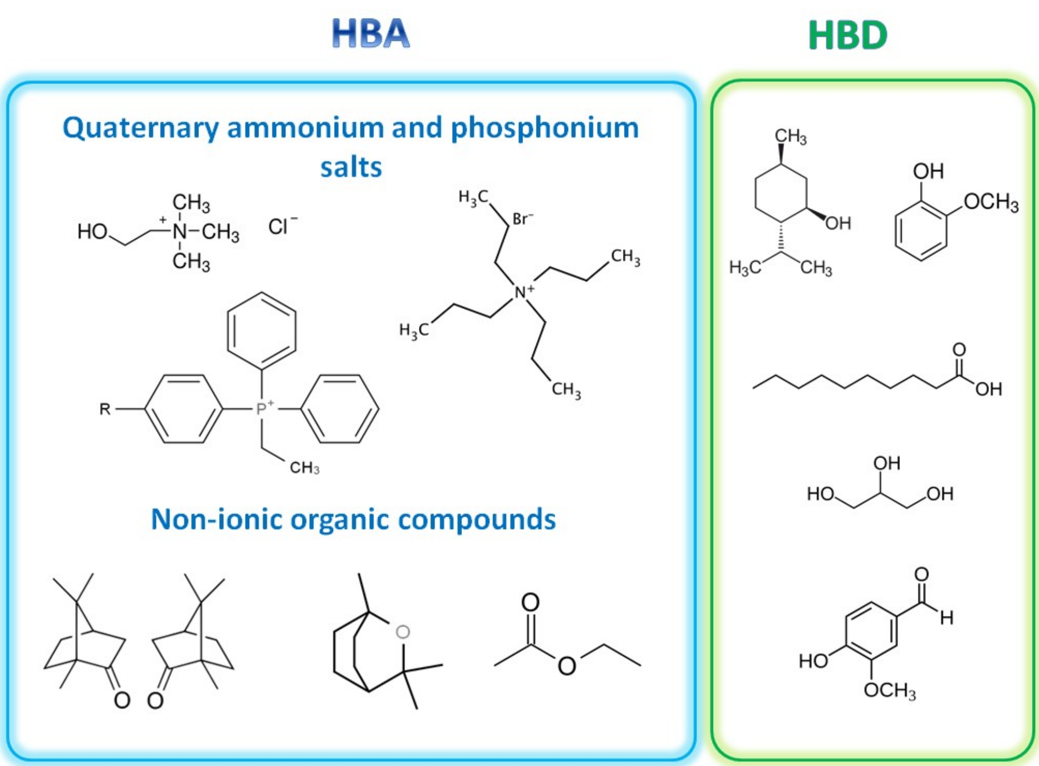

Figure 2: Typical structures of DES components.

2.1. Physicochemical properties of DES

Physicochemical properties such as viscosity, density, conductivity, acidity, surface tension, volatility, melting point, and boiling point depend on the type of DES components, their molar ratio, and the type of bonds between them. Both these parameters and biodegradability, toxicity, and thermal stability are taken into account when choosing the best solvent for analytical techniques.

The hydrophobicity is greater for DES when both components are hydrophobic than when one compound is hydrophobic and the other is hydrophilic. As the chain length increases, the stability of DES in the aquatic environment increases. Deep eutectic liquids by definition have a significantly lower melting point than pure ingredients. The stronger the interaction between the components, the lower the melting point. Melting points below 20°C are particularly advantageous for utility purposes [2]. According to the twelve principles of green chemistry, solvents should be characterized by low vapor pressure. Due to the fact that the main DESs are composed of ionic compounds, they have non-volatile nature.

Density during the extraction process is one of the most important parameters. The most advantageous are large differences in DES and water density (during extraction from an aqueous medium). The greater the difference in density, the easier the phases separate. Ionic DES densities vary from 850 to 980 kg/m^3 while non-ionic DES in the range of 870 to 1091.8 kg/m^3 at 25°C.

Viscosity of DES is another important parameter strongly affected on extraction. Most of DES characterized by relatively high viscosities (>100 mPas) at RT. Viscosity increases as the tetraalkyl quaternary chain increases. Non-ionic DESs composed of monoterpenes have slightly lower viscosities. Their values are usually in the range from 1 to 20 mPas.

Surface tension also plays an important role in the extraction process. DES are characterized by high values of this parameter, which is very advantageous. The greater the surface tension force, the greater the efficiency of mass transfer between the phases [2].

3. Deep eutectic solvents in sample preparation

Due to its green nature, interest in DES is constantly growing and with it the number of possible applications. The traditional liquid-liquid extraction method uses large amounts of organic solvents that DES can replace. So far, DES were successfully applied in conventional liquid liquid extraction (LLE) due to the possibility to structurally tune to facilitate the extraction of vide range of metals including Cr (VI) , Cu (II), ^{111}In (III), and organic compounds i.e. pesticides, organic acids, and alcohols from water samples [2].

However, most of the described application of DES are in microextraction processes, which characterized by small amounts of solvents, at the level of microliters [1-2]. For example head space single drop microextraction was made using DES composed of choline chloride and 4-chlorophenol to extract pesticides from vegetables and fruits [3]. DLLME was successfully made using tetrabutylammonium bromide as a hydrogen bond acceptor and ethylene glycol, glycerol, acetic and formic acids as donors of hydrogen bond [6]. Another type of extraction is solid phase extraction. It can be conducted in a standard way, i.e. with solid sorbents. Solid sorbents can be modified with DES [1-2].

4. Conclusion

Deep eutectic solvents are a very promising class of solvents that allows to replace organic solvents in analytical processes. Research on new materials and their application is constantly being carried out dynamically. They have many attractive functional features and are safe for the environment. They are thermally stable, stable in water, cheap, biodegradable, and less toxic than standard solvents. Moreover, the properties of DES can be controlled by selecting the appropriate components, which makes them more attractive. According to the conducted research, DES can be used very well in the preparation of samples for chemical analysis. Thanks to them, it is possible to selectively separate an analyte from another phase using various extraction methods.

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