Synthetized membranes for ultrasound-assisted solvent extraction of porous membrane packed solid samples

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Keywords
diapers
extraction
membranes
phthalates
PVDF

Abstract
Membranes are becoming more and more popular in analytical chemistry, which is why they are used, among others, in extraction processes. Therefore, this work focuses on the process of synthesizing polyvinylidene fluoride membranes and their optimization. The obtained membranes were used as bags for phthalate extraction in disposable diapers for babies. Extraction was accomplished by method ultrasound-assisted solvent extraction of porous polyvinylidene fluoride membrane packed solid samples. As a result of the research, it was found that the most optimal temperature for the synthesis of membranes was 40 °C. The phthalates were extracted in this process. However, the reproducibility was insufficient.

1. Introduction

Nowadays, a key role in analytical chemistry is the extraction of analytes from samples of complex matrix composition. Unfortunately, analytical methods involving the extraction of components from such samples usually require their dilution or dissolution in a solvent. In order to avoid analytes loss, a new method for direct extraction into a suitable solvent from solid analytes was invented. An interesting and relatively simple method of analyzing different kinds of samples, including solid samples, can be the micro-solid extraction phase protected by a porous membrane (μ-SPE). It consists of packing the sorbent containing the adsorbed analyte in bags equipped with membranes. Unfortunately, in this case, the samples are also diluted or dissolved. An alternative that can solve the problem may be the aforementioned ultrasound-assisted solvent extraction of porous membrane packed solid samples (UA-SEPMPS), in which instead of packing the sorbent, the solid sample is directly packed into a membrane bag and immersed in a suitable solvent. The membrane used for such a process may be a membrane made of polyvinylidene fluoride (PVDF). Polyvinylidene fluoride is a thermoplastic fluoropolymer having a relatively high degree of crystallization. It

has good mechanical, electrical, and thermal properties, and is additionally characterized by high chemical resistance and hydrophobicity. For this reason, it is often used for the production of membranes, e.g., for microfiltration or ultrafiltration. These membranes can be obtained, inter alia, by the method of inversion of the dry and wet phase, in which it is possible to change the temperature parameter. This paper presents the process of obtaining membranes made of polyvinylidene fluoride and the optimization of the parameters of their preparation. The results of properties such as contact angle, thickness, brittleness, and porosity as a function of the membrane preparation temperature are also presented. In addition, the synthesized membranes were applied for the microextraction process of phthalates in disposable baby diapers [1, 2].

2. Experimental

2.1 Reagents and chemicals

To synthesize membranes purity chemical reagents were used. The polymer used for the synthesis was polyvinylidene fluoride, PVDF Solef® (type 6020 Solvay company). 1-Methyl-2-pyrrolidine about purity 99% (Sigma-Adrich) was a solvent, in which polymer was dissolved. For rising membranes isopropanol was used. Kerosene (Thermo-Fisher Scientific) was applied for measuring the porosity of membranes.

2.2 Samples

Commercially available disposable baby diapers of the common brand were used. The bag of diapers was opened prior to analysis.

2.3 Instrumentation

The resistance to wetting with pure water was investigated by measuring the contact angle value (OCA 15 apparatus, Dataphysics). Fourier transform infrared spectroscopy (FTIR) was used to collect spectra of the membranes in the scan range of 400–4000 cm^{-1} in ATR mode with a resolution of 16 cm^{-1} using a Nicolet iS10 FTIR spectrometer (Thermo Scientific Instrument). The thickness of the membrane was measured using an electronic micrometer (Schut).

2.4 Synthesis and optimization procedure

Synthesis membranes were performed by the dry-wet phase inversion method. The general scheme of the synthesis is shown in Fig. 1. The first had to be measured out 12% polymer solution in 1-methyl-2-pyrrolidinone. In this way, 6 grams of polymer polyvinylidene fluoride powder for 50 grams of a solution was

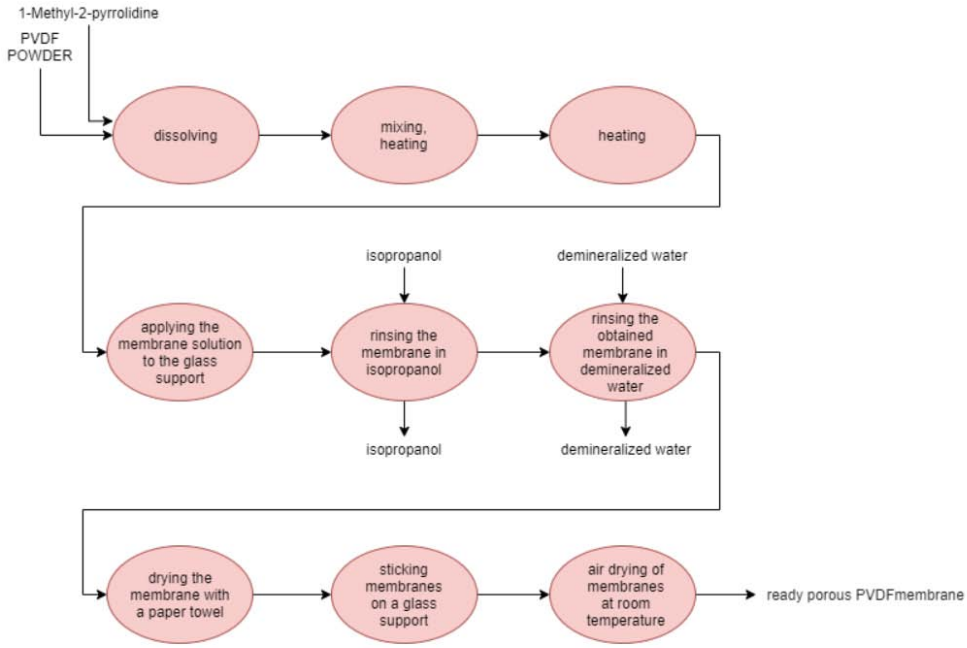

Fig. 1 General scheme for the synthesis of polyvinylidene fluoride (PVDF) membranes by dry-wet phase inversion method.

weighted out. Next, the solution prepared in this way was placed on a mechanical stirrer and mixed and heated to set temperature for about 24 hours. After that time, mixing was stopped to avoid excessive bubbles but heating was held. It was for the next 24 hours. When the solution was homogenized, the polymeric solution was spread onto glass using a special membrane knife set in width 250 µm. After poured, glass with membrane was immersed in isopropanol for 10 minutes in order to promote solid-liquid demixing and next, in demineralized water for 24 hours for thorough rinsing. The next action was drying membranes. Rinsed membranes were pre-drained by paper towel and then, glued to the glass by adhesive tape. It was drying by the air at room temperature, after which it was removed from the glass. The optimization process was based on the temperature changing during mixing and synthesis. The temperature used was 20, 40, and 70 °C. Each membrane was examined in terms of mechanical properties, contact angle, infrared spectrum, thickness, and porosity [3].

3. Results and discussion

The possibility of using membranes for ultrasound-assisted solvent extraction of porous membrane packed solid samples for determination of selected analytes from solid samples directly, shows innovation, however, poses a challenge to

Table 1
Porosity and the contact angle of the obtained polyvinylidene fluoride membranes synthesized at various temperatures.

Temperature of synthesis / °C	Porosity	Contact angle / °
20	0.65±0.04	134.5±1.0
40	0.85±0.02	144.4±3.8
70	0.83±0.02	143.4±1.8

select the appropriate membranes that can be used in the process. In this work, polyvinylidene fluoride membranes were synthesized and applied for extraction for the first time. The membranes were obtained at 20, 40, and 70 °C, each with different properties. Already upon receipt, differences in brittleness and properties of the membranes could be noticed. Membrane synthesized at a temperature of 20 °C, the polymer solution was unevenly solution and in some places differed in density, which was noticeable when pouring the membrane. Thus, the resulting membranes differed in thickness over the entire surface.

After drying, the membranes obtained at 40 °C exhibited the best mechanical properties. They detached easily from the glass, did not tear, showed a uniform thickness, and were not brittle. On the other hand, the membranes obtained at 70 °C dissolved evenly, but after drying they were characterized by high brittleness and were torn already when they were removed from the glass.

The thicknesses of the obtained membranes also varied. The average membrane thickness was 0.041 μm for 20 °C, 0.102 for 40 °C, and 0.094 for 70 °C. So after drying, the thickest membrane turned out to be the one obtained at 40 °C, which could involve showing the best mechanical properties. The thinnest ones turned out to be those obtained at 20 °C, but the thickness varied across the surface. All membranes were applied to the glass with the use of the "Knife for membranes" applicator with a set thickness of 250 μm in each case. The analysis of the IR spectra showed almost identical spectra for all tested membranes, which means that homogeneous products were obtained in all synthesized membranes. The results of the porosity of the obtained membranes are presented in Table 1. The highest porosity was obtained for membranes synthesized at 40 °C and it was 0.85±0.02. The contact angle test showed high hydrophobicity for all membranes. The results of the test are presented in Table 1. The highest contact angle was recorded for membranes produced at 40 °C, it was 144.4°±3.8°, therefore these membranes showed the highest hydrophobicity. The drop size of water used in the test was 4 μL. All of the research carried out during optimization unambiguously allowed to state that the obtained membranes with the best properties were those synthesized at 40 °C, both in terms of mechanical and hydrophobic properties, porosity, and thickness. Therefore, these membranes were applied as a bag in ultrasound-assisted solvent extraction of porous membrane packed solid samples for the selected phthalates extraction from spiked disposable baby diapers.

Furthermore, the sample extract was analyzed by GC-MS. The selected analytes were extracted, however, the repeatability was insufficient.

4. Conclusions

The use of polyvinylidene fluoride polymer membranes to extract analytes from solid samples is an interesting issue. A modern technique ultrasound-assisted solvent extraction of solid samples packed in porous polyvinylidene fluoride membrane, which allows avoiding the dilution or dissolution of the test solids samples in order to perform the extraction seems to be a promising discovery. The results of the research on disposable diapers for babies with the used synthesized membranes after the optimization process showed the effectiveness in the extraction of phthalates. However, due to insufficient repeatability, they require refinement and a series of tests to improve a given method.

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Application of deep eutectic solvents in analytical chemistry

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Keywords
deep eutectic solvents
extraction
green solvents
microextraction

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. 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.

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 adapts 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].

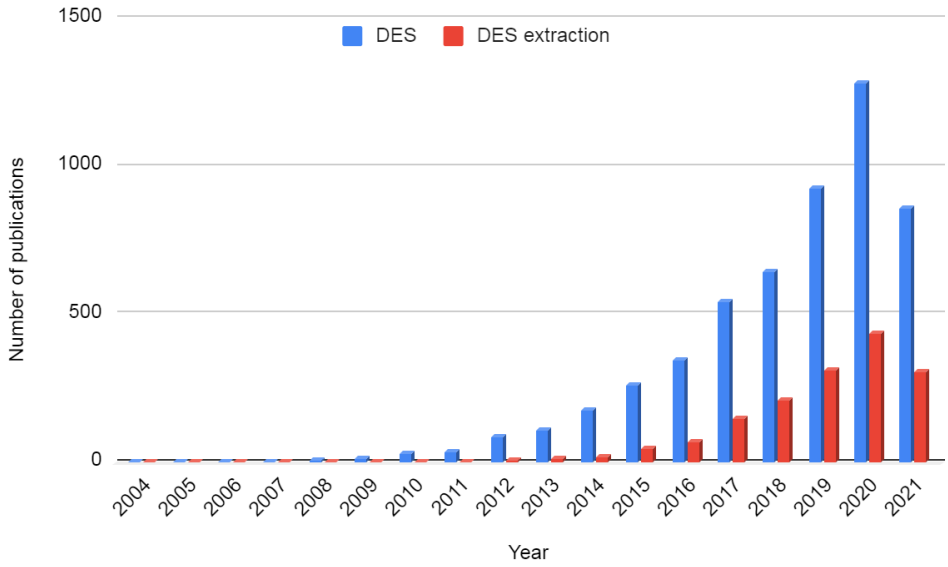

Fig. 1 Number of papers published during 2004–2021 on extraction with the deep eutectic solvents (DES) based on Scopus database (searched keywords: deep eutectic solvents and deep eutectic solvents extraction; accessed on 24.06.2021).

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

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 deep eutectic solvents bind with each other through various interactions, including hydrogen bonding and electrostatic interaction. So, a hydrogen bond donor component and a hydrogen bond acceptor component can be distinguished. Chemical compounds forming deep eutectic solvents 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. Deep eutectic solvents can be hydrophilic or hydrophobic, their nature will be determined by the substrates [7–8].

2.1 Deep eutectic solvents synthesis

There are two main deep eutectic solvents 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. The great advantage of this method is the lack of formation of unfavorable esters due to the process being carried out at room temperature. 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 deep eutectic solvents can be distinguished. By combining quaternary salts with hydrophilic hydrogen bond acceptor, the obtained deep eutectic solvents will have hydrophilic nature. The use of these deep eutectic solvents s 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 deep eutectic solvents increases, the interactions between the components weaken. For this reason, research is conducted mainly on hydrophobic deep eutectic solvents, which will remain stable in the aquatic environment [1]. Hydrophobic deep eutectic solvents can be obtained by mixing a quaternary salt or terpenes (hydrogen bond acceptor) with an appropriate hydrogen bond donor compound. Some compounds can be both acceptor and hydrogen bond donors. Hydrogen bond acceptors based on long-chain ammonium salts are often used in the synthesis of hydrophobic and ionic deep eutectic solvents, as the longer hydrocarbon chain enhances the hydrophobic character. In addition in non-ionic hydrophobic deep eutectic solvents, components from a group of monoterpenes, i.e., camphor, eucalyptol can be used as hydrogen bond acceptor due to their high hydrophobic nature. Long-chain alcohols, acids, amino acids, polyphenols, and sugars are often used as hydrogen bond donor [2]. Examples of hydrogen bond acceptor and hydrogen bond donor are shown in Fig. 2.

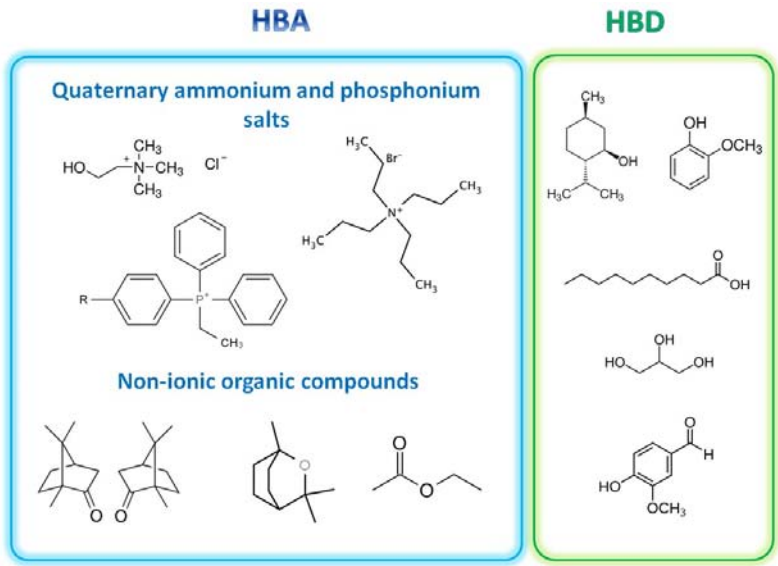

Fig. 2 Typical structures of deep eutectic solvents components: (HBA) hydrogen bond acceptor, and (HBD) hydrogen bond donor.

2.2 Physicochemical properties of deep eutectic solvents

Physicochemical properties such as viscosity, density, conductivity, acidity, surface tension, volatility, melting point, and boiling point depend on the type of deep eutectic solvents 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 deep eutectic solvents when both components are hydrophobic than when one compound is hydrophobic and the other is hydrophilic. As the chain length increases, the stability of deep eutectic solvents 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 deep eutectic solvents 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 deep eutectic solvents and water density (during extraction from an aqueous medium). The greater the difference in density, the easier the phases separate. Ionic deep eutectic solvents densities vary from 850 to 980 kg m^{-3} while non-ionic deep eutectic solvents in the range of 870 to 1091.8 kg m^{-3} at 25 °C.

The viscosity of deep eutectic solvents is another important parameter strongly affected on extraction. Most deep eutectic solvents are characterized by relatively high viscosities (>100 mPas) at room temperature. Viscosity increases as the tetra alkyl quaternary chain increases. Non-ionic deep eutectic solvents 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. Deep eutectic solvents 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 deep eutectic solvents is constantly growing, and with it the number of possible applications. The traditional liquid-liquid extraction method uses large amounts of organic solvents that deep eutectic solvents can replace. So far, deep eutectic solvents 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 applications of deep eutectic solvents are in microextraction processes, which are characterized by small amounts of solvents, at the level of microliters [1–2]. For example head space single drop micro-extraction was made using deep eutectic solvents composed of choline chloride and 4-chlorophenol to extract pesticides from vegetables and fruits [3]. Dispersive liquid–liquid microextraction was successfully made using tetrabutyl-ammonium 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 deep eutectic solvents [1–2].

4. Conclusion

Deep eutectic solvents are a very promising class of solvents that allows the replacement of 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 deep eutectic solvents can be controlled by selecting the appropriate components, which makes them more attractive. According to the conducted research, deep eutectic solvents 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.

Acknowledgments

The research is funded by National Science Centre, Poland within the grant project (No.: 2020/37/B/ST4/02886).

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