DEEP EUTECTIC SOLVENTS AS AN ADDITIVE IN MODIFICATION OF MEMBRANEFOR NANO- AND ULTRA-FILTRATION: PHYSIC-CHEMISTRY CHARACTERISTICS, FTIR STUDY AND ELECTROCHEMICAL BEHAVIOR

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Deep eutectic solvents (DESs) are a new class of solvents that can offset some of the primary drawbacks of typical solvents and ionic liquids. They are synthesized by simply mixing the components that interact with each other through hydrogen bonds, and form a eutectic mixture with a melting point much lower than each component individually. Deep eutectic solvents is usually liquid at temperatures below 100 °C. Thanks to these great advantages, deep eutectic solvents is attracting more and more attention in many areas of research. Very recently, great attention has been paid to new pioneering attempts aiming at deep eutectic solvents into the field of chemical engineering, including membrane science and technology. Even if just a same works have been currently reported in applying deep eutectic solvents in membranes, the consideration on this new type of solvents is continuously growing. New deep eutectic solvents based on choline chloride (ChCl)–lactic acid (1:2 M ratio) was obtained and its electrochemical characteristics was studied. The synthesis of deep eutectic solvents was confirmed by FA nuclear magnetic resonance (NMR) spectrometry method. FTIR study provided further details into hydrogen bonding upon mixing. FTIR results confirmed that H-bonds, occurring between two components in deep eutectic solvents, were the main force leading to the eutectic formation. The frequency at 3221 cm^{-1} can be attributed to the oscillations of the O-H bond in the formation of OH-Cl-ChCl. The main physicochemical characteristics of deep eutectic solutions (density, pH) are determined. The electrochemical behavior was investigated of choline chloride (ChCl)–lactic acid deep eutectic solvent (DES) by cyclic voltammetry. The method of cyclic voltammetry found that the oxidation of deep eutectic solvents is fixed at a potential of $E_{a1} = 0.54$ V.

Keywords: *choline chloride (ChCl)–lactic acid, deep eutectic solvents, ionic liquids*

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1. Introduction

Due to the fast growth of population, critical disposition of water pollution and shortage of healthy water resources, the water problem is turning in to a tension. One of the major problems of modern society is to be able to provide clean water to everyone, or in another words, to develop efficient wastewater treatment processes and simultaneously reduce the hazardousness of the current pollutants present in different kinds of wastewater as a result of domestic, industrial and agricultural water activities. As a result, alternative techniques and materials for large-scale use in water decontamination processes have been considered. Nanofiltration technology has recently gained increased interest in different fields. The membranes used in filtration technology have a number of shortcomings and often use their modification into the casting solution will be an effective and suitable procedure to optimize the structure and morphology of the membrane. A new direction in membrane modification is the use of deep eutectic solvents that play different roles in the kinetics and thermodynamics of the membrane's fabricating process as a characterized result of the performances and structures of the membranes. So, DESs possess different usages in the fields of electrochemistry, polymer synthesis, nanoscale and functional materials and water purification. Deep eutectic solvents (DESs) are green and sustainable solvents having both hydrogen bond donors and acceptors [1-5]. Deep eutectic solvents (DESs) have been successfully used for modification of sorbents, water purification, modification of membrane surfaces. Nevertheless, the uses of DESs in fabrication of membranes have relatively remained unexplored up to now. Very recently, DES-supported membranes have been centered in the attention of researchers in diversified fields from biotechnology, extraction, wastewater purification, and gas separation to energy conservation and storage. However, the first step is the synthesis of deep eutectic solvents and study of these physic-chemistry characteristics.

A wide range of different classes of compounds that can be used for the synthesis of deeply eutectic solvents has led to the complete adaptation of their respective properties as solvents. Liquid systems of an ionic nature, which are obtained by mixing in a certain ratio of some individual organic substances, have a number of practically useful properties, namely a wider range of extraction capacity, thermal and chemical stability, polarity, variability of constituents and electrical conductivity (compared to organic solvents), non-volatility, and incompetence. This complex of valuable DES properties offers great potential for their use in promising elements of the membrane technology and in water purification technologies. As reported by Mohsen [6] to elevated various properties and high selectivity and permeability, the DES-supported membrane has exhibited a high potential ability to be employed as a promising solution for discarding pollutants from polluted water streams and tackling the upcoming water crisis. Hydrophobic deep eutectic solvents (DES) as supported liquid membrane (SLM) for electromembrane extraction (EME) were tested [7]. In this context, this work focuses on the development of deep eutectic solvents (DESs based on choline chloride and carboxylic acid) and evaluations their redox property of for further uses in the membrane technology and in water purification technologies. In the presented study, the basic physicochemical properties of deep eutectic solvent composed of choline chloride (HBA) and lactic acid (HBDs) with 20% (w/w) of initially added water was investigated.

2. Materials and Methods

2.1. Preparation of DES

A DES is often made with a mixture of a salt and a hydrogen bond donor molecule which is able to form bonds with the halide in the salt as shown in Figure 1. Briefly, Choline chloride and different hydrogen bond donor

HBD (Lactic acid) were mixed in sealed 100 mL glass flasks in molar ratios. The mixtures were placed in a round-bottom flask and continuously stirred at 60 °C, 300 rpm in a magnetic stirrer until the mixture formed a clear solution. ChCl (choline chloride, Sigma Aldrich, 98.9% purity) and LA (D,L-lactic acid, Sigma Aldrich, 91.4% purity) were used as received from the commercial suppliers

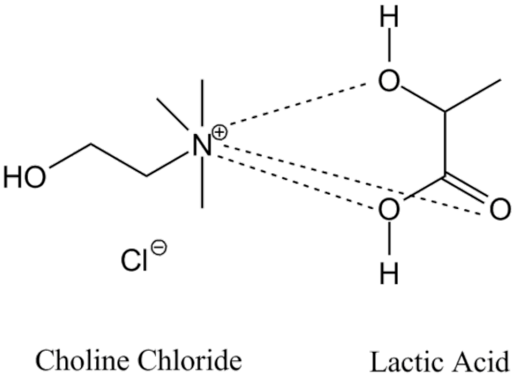

Fig. 1. *Hydrogen bond donor (HBD) and acceptor (HBA) studied in this work lead to the formation of Choline chloride and Lactic acid*

2.2. Characterization of deep eutectic solvents (DES)

The synthesis of DES was confirmed by FA nuclear magnetic resonance (NMR) spectrometry method (Bruker Ascend 300). A nuclear magnetic resonance (NMR) spectrometer operating at 300 MHz was used to record the 1H NMR spectra of the NADESs. All samples were dissolved in D_2O. The chemical shift corresponding to the methyl group peak has been used as a reference for the 1 H NMR spectra. The water content of the DESs was measured using a Mettler Toledo V30S KF titrator where HYDRANAL−Composite 5 and HYDRANAL−Methanol dry (Honeywell, Fluka) were used as the titrant and medium, respectively. The density of synthesized DES was assayed by weighting1 cm^3 of DES at analytical balances (Mettler Toledo, Spain) withan accuracy of ± 0.005 $g\times cm^{-3}$ at room temperature. The results were presented as $g\times cm^{-3}$.The pH values were determined using a digital pH-meter in therange of 0–14.

Fourier transformed infrared spectrum (FTIR) spectra of the DESs were obtained using a Bruker Tensor 27 (Bruker Corp, Massachusetts, USA). A total of 14 scans were measured at 4 cm^{-1} resolution with a scan rate of 22 scans/min. Measurements were done between 650 and 4000 cm^{-1} and using air as a reference.

Cyclic voltammograms were recorded as was previously reported. Working electrode was glassy carbon, the auxiliary electrode – platinum plate and the reference electrode – saturated silver chloride electrode (E = 0.2 V/NHE). The working electrode was cleaned with organic solvent prior and polished with filter paper before each test. Cyclic voltammograms were measured in the potential range –1…+1 V/SSCE with a scan rate of 100 mV/sec.

3. Results and Discussion

In general, investigated DES had higher densities than water. The density of the system under study was 1.14 $g\cdot cm^{-3}$. DES with organic acids (Lactic acid) as HBD showed the strongest acidic behavior. The measured pH values of Choline chloride:Lactic acid 0.20 w/w solutions were 1.55.

NMR on the DESs. 1NMR analysis was performed for the obtained NADES. The peak of LA (Lactic acid oligomer) at 1.48 ppm, has an integral of value 2.11, while at 3.44 ppm, labeled with number 9 the peak of [Ch][Cl] has an integral value of 2.00. Thus, the molar ratio of the [Ch][Cl]:LA is indeed 1:2. A peak around 1.4 ppm is present, which is not related to the pure NADES components; hence it could be attributed to a 30% of water in the system (Fig. 2). The measured pH values of Choline chloride:Lactic acid solution was 1.55 respectively

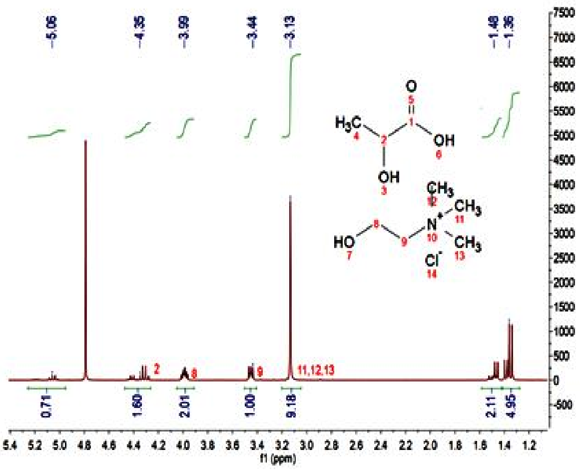

Fig. 2. *1H NMR spectrum of the DES [Ch][Cl]:LA*

FTIR is an important tool to analyze the supramolecular structure of DESs. It is possible to identify the structure and characteristics of chemical bonds using FTIR frequencies. The obtained result suggest that solvent ChC:LA showed a broad spectrum in the range of ~3700–2600 cm^{-1}, which could be attributable to the stretching vibration band of acidic -OH groups as well as to the strong hydrogen bond formation between the Choline chloride and lactic acid. The frequency at 3221 cm^{-1} (Fig. 3) is assigned to the OH stretching frequency associated with OH-Cl- of ChCl. The OH stretching region of oxalic acid contains broad overlapping bands centered around 3420 cm^{-1} that is typical of carboxylic acid forming strongly bonded dimer rings through intermolecular H-bonding between C-O and O-H groups. The outline of the bond may be due to the combined bonding of choline chloride and lactic acid molecules overlapping in the O-H and N-H bond [5]. Two weak peaks were observed at 2987 cm^{-1} in DES, indicating C-H stretching bonds, but shifted to a slightly lower wave number.

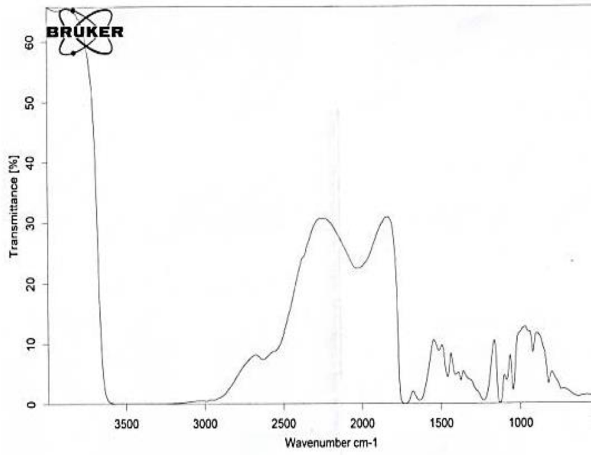

Fig. 3. *FTIR diagram of the tomato DES*

From the spectroscopy data, it can be inferred that during the formation of DES, the strong Choline OH…Cl and COOH… COOH bonds in ChCl and LA breakdown to produce a newstronger in-termolecular COOH…Cl bonds, which explain the stability of liquid phase, lowering of melting point and high viscosity of the LA. As largely evidenced in the literature [1-5], the creation of the typical DES network involves weak interactions (e.g. hydrogen bond and Van Der Waals interaction) that the chloride anion establishes with both the quaternized nitrogen atom of choline and the -OH moieties of the HBD. In the present case, being LA the HBD, the (at least partial) disruption of the “like-like” (LA-LA) interaction is required to establish the “like-unlike” network [8]. It is also suggested that multiple types of H bonds in form of OH (LA)-Cl-, OH (ChCl)-Cl- and LA-LA can be present in the resultant DES.

Cyclic voltammetry of the DES obtained on a glassy carbon electrode. Potential scan rate – 100 mV/s, t = 25.

The electrochemical behavior was investigated of choline chloride (ChCl)–Lactic acid deep eutectic solvent (DES) by cyclic voltammetry (CV). The results of cyclic voltammetry are presented in Fig. 4, and the main parameters are presented Table 1. In the cyclic voltammograms of DESs, the oxidation peaks were observed at the 200 and 500 mV/SSCE potentials. The cyclic voltammogram for the DES showed no clear reversible peaks but only gave a shoulder and a monotonously increasing peak (Fig. 4).

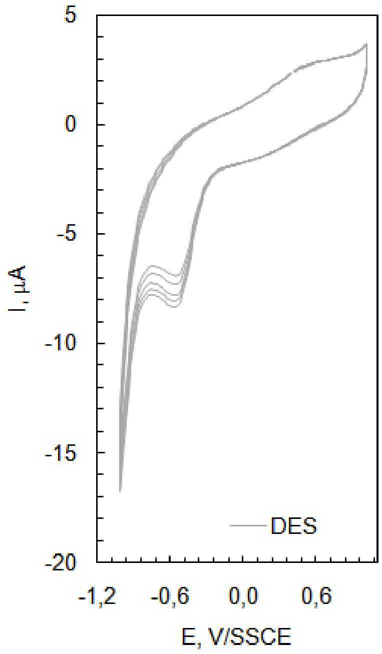

Fig. 4. *Cyclic voltammetry of the DES on a glassy carbon electrode. Potential scan rate – 100 mV/s, t = 25 ℃*

The topscan represents the oxidation of the system, generating a positive (anodic) current (Ia= µA), peaking at a particular electrode potential (Ea1 = 0.54 V). Considering the DES formulation, the oxidation of chloride ions could be responsible for the anodic limit; on the other hand, the cathodic limit may be ascribed to the reduction of carboxylic moieties. The results obtained show that the obtained des is an electrochemically stable system and can be used in the future in the membrane technology and in water purification technologies.

4. Conclusions

In the present paper a first study of the electrochemical properties of DES, based on choline chloride (ChCl)–lactic acid (1:2 M ratio), is carried out. Conclusions to each subparagraph should be given in a separate paragraph. The nuclear magnetic resonance (NMR) spectrometry method are combined with FTIR spectroscopy study showed that in the mixture are dominated by ChCl–lactic acid eutectic interactions by hydrogen bonding.

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ГЛИБКО ЕВТЕКТИЧНІ РОЗЧИННИКИ ЯК МОДИФІКУЮЩИЙ КОМПОНЕНТ ДЛЯ НАНО- ТА УЛЬТРАФІЛЬТРАЦІЙНИХ МЕМБРАН: ФІЗИКО-ХІМІЧНА ХАРАКТЕРИСТИКА, ФУР'Є-СПЕКТРОСКОПІЯ ТА ЕЛЕКТРОХІМІЧНІ МЕТОДИ ДОСЛІДЖЕННЯ

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Глибоко евтектичні розчинники (ГЕР) - це новий клас розчинників, які можуть компенсувати деякі з основних недоліків типових розчинників та іонних рідин. Їх синтезують шляхом простого змішування компонентів, які один з одним взаємодіють за допомогою водневих зв'язків, і утворюють евтектичну суміш з температурою плавлення значно меншою, ніж у кожного компонента індивідуально. Глибоко евтектичні розчинники зазвичай рідкі за температури нижче 100 °С. Завдяки цим чудовим перевагам, глибоко евтектичні розчинники привертають до себе все більшу увагу у багатьох областях досліджень. Зовсім недавно велика увага була приділена інноваційним спробам, спрямованим на використання глибоко евтектичних розчинників у галузі хімічної інженерії, а саме в технології модифікації мембран. Оскільки глибоко евтектичні розчинники є дешевшими та простішими в приготуванні у порівнянні з іншими типами іонних рідин. Отримано нові глибоко евтектичні розчинники на основі холін хлориду та молочної кислоти (співвідношення 1:2М), вивчено їх електрохімічні характеристики. Успішність проведеного синтезу та отримання іонної рідини було підтверджено методом спектрометрії ядерного магнітного резонансу (ЯМР). При синтезі глибоко евтектичних розчинників методом інфрачервоної спектроскопії додатково підтверджено формування водневого зв'язку. Частоту при 3221 см$^{-1}$ *можна віднести до коливань зв'язку О-Н при формуванні OH-Cl-ChCl. Окисно-відновлювальну характеристику отриманої іонної рідини системи холін хлорид-молочна кислота досліджували методом циклічної вольтамперометрії. Визначено основні фізико-хімічні характеристики глибоко евтектичних розчинників (густина, pH). Методом циклічної волтамперометрії встановлено, що окиснення глибоко евтектичного розчинника, фіксується за потенціалу* $E_{a1} = 0{,}54$ *В.*

Ключові слова: *хлорид холіну - молочна кислота, глибоко евтектичні розчинники, іонні рідини*