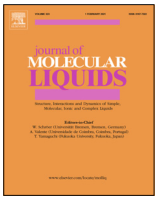
Journal of Molecular Liquids 365 (2022) 120158

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq



Magnetic deep eutectic solvents – Fundamentals and applications

Patrycja Makoś-Chełstowska [a,b,*], Massoud Kaykhaii [a], Justyna Płotka-Wasylka [c,d], Miguel de la Guardia [e]

[a] *Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdansk University of Technology, 80–233 Gdańsk, Poland*
[b] *EcoTech Center, Research Centre, Gdańsk University of Technology, G. Narutowicza St. 11/12, 80-233 Gdańsk, Poland*
[c] *Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 80-233 Gdańsk, Poland*
[d] *BioTechMed Center, Research Centre, Gdańsk University of Technology, G. Narutowicza St. 11/12, 80-233 Gdańsk, Poland*
[e] *Department of Analytical Chemistry, University of Valencia, Dr. Moliner 50, 46100, Burjassot, Valencia, Spain*

ARTICLE INFO

Article history:
Received 17 May 2022
Revised 25 July 2022
Accepted 19 August 2022
Available online 24 August 2022

Keywords:
Magnetic deep eutectic solvents
Green solvents
Microextraction
Catalyst

ABSTRACT

Magnetic deep eutectic solvents (MDES), a relatively new subclass of conventional deep eutectic solvents (DES) containing additional paramagnetic components in their structure. MDES exhibit a strong response toward external magnetic fields, thus they can improve many industrial and analytical applications. In addition, this new group of solvents present unique physicochemical properties that can be easily tuned by selecting the appropriate ingredients for MDES synthesis. Therefore, the reported studies on properties and applications have increased in recent years. This review highlights the structures and mechanism of MDES formation, methods of synthesis, basic physicochemical properties, including melting point/freezing point, decomposition temperature, magnetic susceptibility, dynamic viscosity, density, ionic conductivity surface tension, toxicity, and hydrophobic/hydrophilic character, together with current application in analytical and industrial methods/procedures. Moreover, advantages, limitations, and future perspectives of the application MDES are critically discussed. We hope that this review will inspire many new perspectives and developments in the field of MDES applications.

1. Introduction

Deep eutectic solvents (DES) were discovered in 2003 [1]. Typically, DES are prepared by a simple combination of two chemical compounds from which one acts as hydrogen bond donor (HBD), and the second one as hydrogen bond acceptor (HBA). The formation of specific interactions between HBA and HBD, including hydrogen bonding and electrostatic interactions, leads to a large melting point depression upon the formation of DES. In most cases, pure DES components are solid, while the eutectic mixture is a liquid at room temperature (RT) [2,3].

Magnetic deep eutectic solvents (MDES) are considered a special category of conventional deep eutectic solvents. MDES consists of two or three substances, including HBA, HBD and an additional magnetic component (MC) as metal chloride of i.e. iron ($FeCl_3$), manganese ($MnCl_2$), gadolinium ($GdCl_3$), cobalt ($CoCl_2$), nickel ($NiCl_2$) [4]. Procedures of MDES synthesis and the assumptions of the mechanisms of interaction between the components are similar to conventional eutectic mixtures. In addition, MDES have similar unique properties as conventional DES. However, MDES also exhibit a strong susceptibility to external magnetic fields [5]. The magnetic properties are particularly advantageous in separation techniques i.e. extraction, microextraction, absorption, and adsorption due to the fact that application of MDES can accelerate, streamline and increase the efficiency of processes, as well as reduce the number of necessary steps [5–9].

Therefore, research on new MDES systems, their properties and potential applications is becoming highly attractive. The growing interest in MDES is illustrated by the graph of the number of published papers during a period of 2010–2022 (Fig. 1). Due to simpler

---

Abbreviations: BTPB, butyltriphenylphosphonium bromide; ChCl, Choline chloride; CTAB, Cethyltrimethylammonium bromide; DES, Deep eutectic solvents; DTAB, Dodecyltrimethylammonium bromide; FP, Freezing point; FT-IR, Fourier transform infrared spectroscopy; GC/MS, Gas chromatography–mass spectrometry; GS, 1,3 bis(dodecyldimethylammonio) 2 hydroxypropane dichloride; HBA, Hydrogen bond acceptor; HBD, Hydrogen bond donor; HPLC, High Performance Liquid Chromatography; LPME, Liquid phase microextraction; LOD, Limit of detection; LOQ, Limit of quantification; MC, Magnetic component; MDES, Magnetic deep eutectic solvents; MIP, Molecularly imprinted polymer; $MnCl_2$, Manganese (II) chloride; RSD, Relative standard deviation; STAB, Stearyltrimethylammonium bromide; TBAB, Tetrabutylammonium bromide; TBAC, Tetrabutylammonium chloride; TBPB, Tetrabutylphosphonium bromide; THDPB, trihexyltetradecylphosphonium bromide; TOAB, Tetraoctylammonium bromide; TTAB, Tetradecyltrimethylammonium bromide; UALLME-DES, ultrasound-assisted liquid-liquid microextraction based DES.

* Corresponding author.
E-mail address: patrycja.makos@pg.edu.pl (P. Makoś-Chełstowska).

https://doi.org/10.1016/j.molliq.2022.120158
0167-7322/

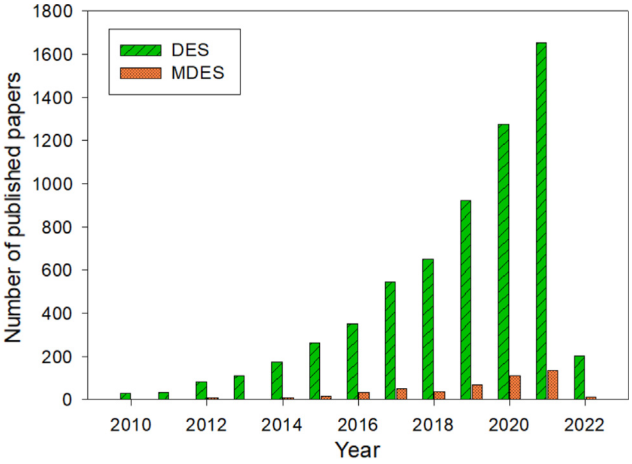


Fig. 1. Number of published papers per year from 2010 to 2022. The graph was build using the Scopus platform, from the topics deep eutectic solvents and magnetic deep eutectic solvents. Access date: 21.01.2022.

and shorter synthesis, the majority of eutectic complexes are still conventional deep eutectic solvents. There is still little information in the literature on the mechanisms of MDES formation, their physicochemical properties and potential applications. To date, only a few MDES combinations have been studied in detail. For the first time in 2017, Khezeli and Daneshfar prepared magnetic complexes consisting of choline chloride:phenol: $FeCl_3$ and choline chloride: ethylene glycol: $FeCl_3$, which they called magnetic deep eutectic solvents [10]. The authors studied in detail the physicochemical and structural properties of the new compounds and applied them as new solvents for the extraction of thiophene from fuels in the ultrasound-assisted liquid–liquid microextraction process. However, the first MDES consisting of choline chloride: ethylene glycol: $MgCl_2$ and choline chloride: $MgCl_2{:}6H_2O$ were published in 2011 [11,12]. The magnetic properties of the published compounds have not been determined. Only the structural and rheological properties, including viscosity, density, surface tension, and thermal properties of new complexes, were determined. Therefore, the authors included them in the group of conventional ionic liquids.

The present review focuses on the structure, synthesis, physicochemical properties (i.e. melting point/freezing point, decomposition temperature, magnetic susceptibility, dynamic viscosity, density, ionic conductivity surface tension, toxicity, and hydrophobic/hydrophilic character), and current applications of magnetic deep eutectic solvents in analytical as well as industrial methods. In addition, advantages, limitations, and future perspectives of the application MDES are also discussed.

2. Structures and preparation of MDES

2.1. Structures of magnetic deep eutectic solvents

The structures of the main components commonly used for MDES preparation are shown in Fig. 2. Most MDES consists of quaternary ammonium/phosphonium salts (i.e. Tetraoctylammonium bromide (TOAB), Tetrabutylphosphonium bromide (TPAB), Tetrabutylammonium bromide (TBAB), Tetrabutylammonium chloride (TBAC), Butyltriphenylphosphonium bromide (BTPB), Stearyltrimethylammonium bromide (STAB), Tetrabutylphosphonium bromide (TBPB), Trihexyltetradecylphosphonium bromide (THDPB), Tetradecyltrimethylammonium bromide (TTAB), and Choline chloride (ChCl) that act as a hydrogen bond acceptors. They are well known substances commonly used in the synthesis of conventional DES [13–15]. As HBD, carboxylic acids, sugars, phenols, glycols, and amides are commonly used. However, most of these compounds can be used not only as HBA but also as HBD due to the characteristic group i.e. = O, –COOH. As the third component, chloride salts with paramagnetic properties are used. Each one of these components is cheap, readily available, and they are characterized by low toxicity.

During MDES preparation, strong hydrogen bonds and weaker electrostatic interactions between the HBA, HBD, and MC components are formed. This leads to a lower melting point of the new MDES compared to the individual components. There are six basic types of MDES structures that are shown in Fig. 3, which is a modified version of the DES classification [16].

Based on the published works, it can be concluded that in the I and II groups, the MC component is the central point in the MDES structure to which the other components (HBA and HBD) are attached. In 2021 Peng et al., based on density functional theory and Fourier-transform infrared spectroscopy analysis (FTIR), explained the mechanism of lauric acid:decanoic acid:$MnCl_2$ (1:2:0.5 M ratio) formation. In MDES, Mn atom forms strong coordination bonds (<2.1 Å) with the oxygen atom from –COOH group of two molecules of decanoic acid and lauric acid. In addition, Cl atoms attract to hydrogen atoms from –COOH groups forming strong hydrogen bonds, between acids and MC [17]. In another work, based on the structure of MDES composed of ChCl, phenol, and $FeCl_3$ in 1:2:1 M ratio (ChCl:phenol:$FeCl_3$), and ChCl:EG:$FeCl_3$ (1:4:1) authors suggested that chloride atom from ChCl joins to $FeCl_3$ and form $FeCl_4^-$ ion. After that, chloride atoms form hydrogen bonding with –OH groups of EG and phenol [10]. The III and IV groups of MDES are simple complexes of two components, which consist of HBA or HBD and a salt with paramagnetic properties. According to the basic classification of DES, these types of MDES can be classified as group $Cat^+X^- + zMCl_x$ or $MCl_x + zRZ$, depending on the type of components used to synthesize. The mechanism for the formation of MDES is exactly the same as conventional DES [13,18]. The V and VI groups consist of HBA and hydrated magnetic components, and a mixture of HBA, HBD, and hydrated MC.

2.2. Preparation

In most works, the MDESs are prepared in two steps. In the first stage, pure deep eutectic solvents are obtained. This step consists in mixing two substances in appropriate molar ratios. The mixture is then mixed together at an elevated temperature (typically from 40 to 80 °C) until clear liquids are obtained. The resulting DES is then cooled to room temperature, according to standard procedure [1,2,4,17]. In the next step, the obtained DES is mixed with different metal chloride (MC) in appropriate molar ratios, and then a small amount of volatile solvent, i.e. dichloromethane, is added. Everything is mixed for about 24 h. After evaporating under reduced pressure the MDES is obtained [4,17]. A similar procedure can be used for the synthesis of IV type of MDES. The procedure consists in mixing quaternary ammonium salts, MC, and ethanol in appropriate molar ratios, under N_2 atmosphere, at room temperature for several hours, and then evaporating the solvent, and drying in a vacuum oven at 80 °C [19]. This method consists of several steps, and the entire procedure takes up to several hours. Compared to the preparation of conventional DES, it is much longer and requires more work. In addition, the necessity to use volatile and toxic solvents means that the obtained MDES cannot be classified as green solvents.

In the literature data, there is also a one-step (one-pot) procedure for the preparation of MDES available. In this method, there is no need to use volatile solvents, and the entire procedure is slightly different from the standard procedure for the preparation of conventional DES. The procedure consists in simply mixing the

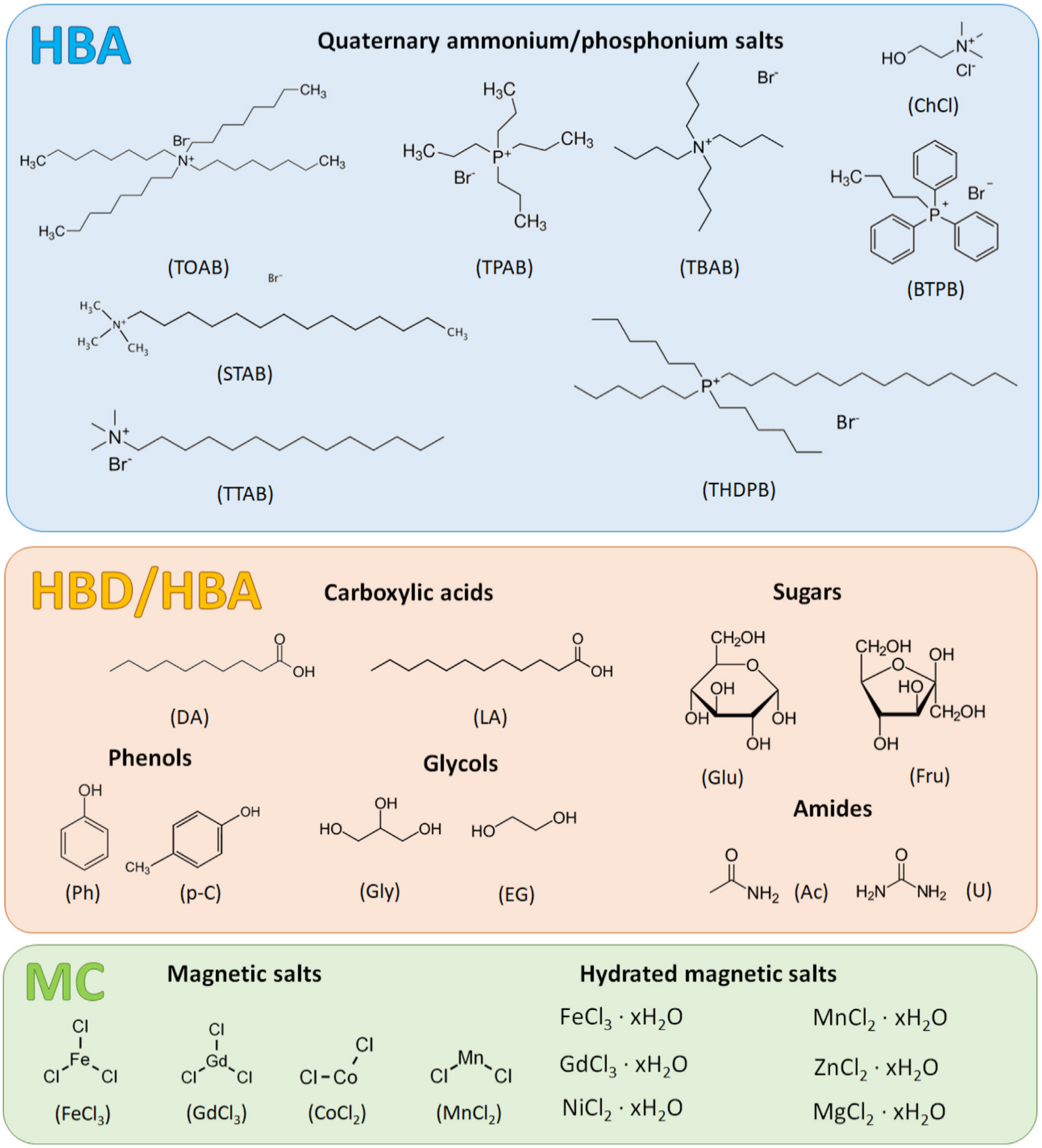


Fig. 2. Typical HBA, HBD, and MC structures in magnetic deep eutectic solvents complexes.

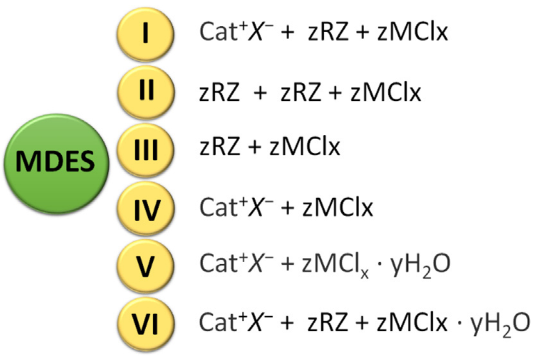


Fig. 3. Modified classification of MDES (where: M - Zn, In, Sn, Al, Fe, Cr, Ni, Cu, Fe, Co; z,y – number of molecules; RZ – compounds with active groups of OH, COOH, $CONH_2$.

two or three components HBA, HBD, and MC at a proper molar ratio at a higher temperature (about 80 °C) until the formation of clear and homogeneous liquid [10,20–22]. The great advantage of this method is that there is no need to purify the final product. In addition, the procedure is much less complicated.

Another way to prepare magnetic DES is the simultaneous synthesis and extraction, the so-called "in situ" method. In the first step, the conventional DES are prepared in the appropriate molar ratios according to standard procedure [1,2,4,17]. After that, the obtained DES is introduced into an aqueous sample. The analytes are extracted to pure DES. Then an appropriately weighed portion of iron chloride is added to the solution. After mixture shaking, magnetic DES is formed in the solution [23]. In this approach, the stages of MDES preparation and extraction are significantly reduced, which significantly shortens the entire procedure. However, no structural studies of the obtained MDES have been performed so far. It is still unknown whether hydrogen bonds are formed solely between the components of MDES, or between water and MDES.

Other methods used in the synthesis of conventional DES include mixing in an extruder [24], freeze-drying method [25], and grinding in a mortar [26]. However, they have not been used for the synthesis of MDES so far.

3. Physico-chemical properties

The physico-chemical properties of MDES largely depend on the components used for the synthesis (HBA, HBD, MC) and their stoichiometry. Even a small change in the proportion of components can significantly affect parameters, such as density, viscosity, melting (freezing) point, decomposition point, conductivity, magnetic properties, hydrophobicity, or hydrophilicity. This is an unquestionable advantage of MDES due to the possibility of adjusting parameters depending on further applications. Therefore, practical application of MDES requires knowledge of the basic physicochemical properties. In this section, the main physicochemical features of MDES are discussed and summarized in Table 1.

3.1. Melting point/freezing point

The melting point/freezing point is a key parameter if a new complex has to be classified as a solvent. Among the previously known DES and MDES, many systems have melting points above room temperature. However, only a small group is characterized by a low melting point [2,27–29]. Most of the processes in which MDES can be used are carried out at room temperature. Therefore, only complexes that are liquids at room temperature are considered as useful DES in most analytical and industrial applications, i.e. separation techniques. Only some applications require higher melting points than room temperature to be employed e.g. electrochemical capacitors [30]. According to the definition of DES, it is a mixture of two or more compounds, the melting point of which is much lower than that of the components from which it was obtained. This decrease in melting point comes from a specific interaction, i.e. hydrogen bonds or van der Waals between components. The two-component system can be described by the simple phase diagram (Fig. 4a). However, most MDES consist of three chemical compounds, and the phase diagram is much more complicated and requires a big number measurements (Fig. 4a). Therefore, there are no examples of such a plot relating to MDES in the literature, and only a few studies show phase plots for conventional ternary DES [31,32].

The melting point of two-component MDES highly depends on components used for MDES synthesis. The melting point of MDES composed of quaternary ammonium salts and MC are relatively high and only few complexes have melting point below 25 °C i.e. ChCl:$ZnCl_2$ (2:1), TPAB:$FeCl_3$ (1:1), TBPB:$FeCl_3$ (1:2) which are 23, 15.7, and 15.7 °C, respectively [19]. This is probably due to the fact that pure quaternary ammonium salts are characterized by high MP. In addition the melting point of MDES increases with increasing tetraalkyl ammonium/phosphonium quaternary chain. However, there is no dependency regarding the molar ratio of quaternary ammonium salts to MC concerning the melting point. In some systems, an increase in MC content in the MDES structure increases melting point, and in some systems, a decrease in melting temperature can be observed. Three-component systems are characterized by similar melting points, which are in the range from 11.2 to 13.2 °C. In comparison with conventional DES, melting point of MDES are slightly higher. For example, melting point of TOAB: decanoic acid (1:2) is 8.95 °C [33], while for TOAB: decanoic acid:$MnCl_2$ (1:2:1) and TOAB: decanoic acid:$CoCl_2$ (1:2:0.5) are 11.2 and 12.5 °C, respectively [4]. This is probably due to the relatively high melting points of the magnetic components, as well as the weakening of the hydrogen bonds in the DES structure. MDES composed of non-ionic substances such as urea, acetamide, ethylene glycol, 1,6 – hexanediol, in combination with $ZnCl_2$ have low melting points in the range from −30 to 9 °C. This is in line with the results for conventional DES [18]. Another solution to achieve low melting points of MDES is to add water. However, there is not enough information on the exact melting points obtained when water is added to the MDES. Moreover, some MDES have a hydrophobic character, therefore the addition of water does not reduce their melting point temperature.

3.2. Decomposition temperature

The decomposition temperature of MDES is an important parameter from the point of view of their use in high-temperature processes. At high temperatures, changes in the structure of MDES, phase changes, breakdown of hydrogen bonding, and electrostatic interaction between HBA, HBD, and MC may occur. Hence, the assessment of the thermal stability of MDES provides information on the temperature at which the solvent can be used without structure changes [34,35].

The decomposition temperature of the three-component MDES is in general higher than that of the conventional DES. For example, DES composed of Tetraoctylammonium bromide (TOAB) and decanoic acid in 1:2 M ratio is characterized by a decomposition temperature of 207.66 °C [33]. Whereas, the decomposition temperatures of TOAB:decanoic acid:$CoCl_2$ (1:2:0.5) and TOAB: decanoic acid:$MnCl_2$ (1:2:1) are respectively 440.6 and 390.6 °C [4]. Other ternary systems composed only of non-ionic substances (i.e. lauric acid:decanoic acid:$MnCl_2$ (1:2:0.5), and lauric acid:decanoic acid:$CoCl_2$ (1:2:0.8)) also have a high degradation temperature above 380 °C. However, there is no information in the literature about these temperatures for conventional DES. Two component MDES also have higher decomposition temperatures than pure substances used in the synthesis. The decomposition temperatures for DTAB:$FeCl_3$ (1:1), TTAB: $FeCl_3$ (1:1), CTAB: $FeCl_3$ (1:1), STAB: $FeCl_3$ (1:1), acetamide:$MnCl_2{\cdot}4H_2O$ (7:1), glycerol: $MnCl_2{\cdot}4H_2O$ (3:1), D(+)-glucose: $MnCl_2{\cdot}4H_2O$ (1:1), D(-)-fructose: $MnCl_2{\cdot}4H_2O$ (1:1) are respectively 231, 226, 223, 212, 193, 146, 103, 108 °C. These values are higher than decomposition temperature of separate components used for MDES preparation [19,36]. This means that the new bonds between the components of MDES are strong enough to form stable complexes that can be used in high temperature processes without significant changes in the structures and properties of MDES.

3.3. Density

The density of solvents is one of the fundamental thermophysical properties in order to be employed in separation processes. The density of most conventional deep eutectic solvents is higher than that of water and is between 1.0 g/cm^3 and 1.35 g/cm^3 at 298.15 K [18,37]. MDES density values are also mainly greater than water. For the two-component MDES densities are in the range from 1.195 to 1.63 g/cm^3 [12,19,38–40]. However, for the ternary MDES i.e. TOAB: decanoic acid:$CoCl_2$ (1:2:0.5), TOAB: decanoic acid: $MnCl_2$ (1:2:1), lauric acid: decanoic acid:$MnCl_2$ (1:2:0.5), and lauric acid: decanoic acid:$CoCl_2$ (1:2:0.8) the densities are close to water density (0.948 – 1.088 g/cm^3). Two-component MDES composed of BTBAB and various magnetic components are characterized by similar densities [41]. To obtain a good phase separation in extraction processes, the densities of the aqueous and organic phases should be significantly different. Therefore, densities of MDES that are close to that of water is unfavorable for the separation of chemical compounds from aqueous samples. The values of

Table 1
Physicochemical properties of magnetic deep eutectic solvents.

HBA	HBD	Magnetic component (MC)	Molar ratio (HBA:HBD: MC)	Molecular weight, M_W [g/mol]	Magnetic susceptibility [emu·goe^{-1}]	Viscosity at 25 °C mPa·s (cP)	Density at 25 °C (g·cm^{-3})	Melting point/ freezing point [°C]	Decomposition temperature [°C]	Hydrophobicity	Conductivity at 25 °C, σ [µS/ cm]	Surface tension γ (mN m^{-1})	Ref.
TOAB	decanoic acid	$MnCl_2$	1:2:1	1017.2	$3.85\cdot10^{-5}$	2.864×10^{5}	0.9478	11.2	390.6	Yes	N/D	N/D	[4]
TOAB	decanoic acid	$CoCl_2$	1:2:0.5	956.2	$1.31\cdot10^{-5}$	2.915×10^{4}	0.9689	12.5	440.6	Yes	N/D	N/D	[4]
ChCl	phenol	$FeCl_3$	1:2:1	490.0	$0.546\cdot10^{-6}$	N/D	N/D	N/D	N/D	No	N/D	N/D	[10]
ChCl	p-cresol	$FeCl_3$	1:3:1	593.9	$0.165\cdot10^{-6}$	N/D	N/D	N/D	N/D	Yes	N/D	N/D	[20]
ChCl	ethylene glycol	$FeCl_3$	1:4:1	524.2	$5.14\cdot10^{-6}$	N/D	N/D	N/D	N/D	No	N/D	N/D	[10]
Lauric	acid	decanoic acid	$MnCl_2$	1:2:0.5	607.7	$2.65\cdot10^{-5}$	437.01	1.0853	12.5	388.5	Yes	N/D	N/D
[17]													
Lauric	acid	decanoic acid	$CoCl_2$	1:2:0.8	648.7	$2.14\cdot10^{-5}$	1759.7	1.0876	13.2	498.9	Yes	N/D	N/D
[17]													
ChCl	glycerol	$MgCl_2$	1:2:0.04	330.3	N/D	175 [e]	1.11	< RT	N/D	No	2090 [e]	N/D	[45]
ChCl	urea	$MgCl_2$	1:2:0.04	266.2	N/D	245 [e]	1.102	< RT	N/D	No	2900 [e]	N/D	[45]
ChCl	ethylene glycol	$MgCl_2$	1:2:0.04	270.2	N/D	60 [e]	1.131	< RT	N/D	No	5000 [e]	N/D	[45]
ChCl	ethylene glycol	$MgCl_2$	1:2:0.2	296.2	N/D	60 [d]	N/D	< RT	120	No	9100 [d]	59 [d]	[11]
ChCl	ethylene glycol	$MgCl_2$	1:2:0.3	312.4	N/D	70 [d]	N/D	< RT	120	No	8300 [d]	62 [d]	[11]
ChCl	ethylene glycol	$MgCl_2$	1:2:0.4	328.6	N/D	80 [d]	N/D	< RT	120	No	7100 [d]	65 [d]	[11]
ChCl	ethylene glycol	$MgCl_2$	1:2:0.5	344.9	N/D	110 [d]	N/D	< RT	120	No	6400 [d]	67 [d]	[11]
ChCl	ethylene glycol	$NiCl_2{\cdot}6H_20$	1:2:1	501.4	N/D	96.78 [c]	N/D	< RT	N/D	No	N/D	N/D	[46]
ChCl	ethylene glycol	$NiCl_2{\cdot}9H_20$	1:2:1	555.4	N/D	48.05 [c]	N/D	< RT	N/D	No	N/D	N/D	[46]
ChCl	ethylene glycol	$NiCl_2{\cdot}12H_20$	1:2:1	609.4	N/D	7.15 [c]	N/D	< RT	N/D	No	N/D	N/D	[46]
ChCl	ethylene glycol	$NiCl_2{\cdot}15H_20$	1:2:1	663.4	N/D	4.05 [c]	N/D	< RT	N/D	No	N/D	N/D	[46]
ChCl	ethylene glycol	$NiCl_2{\cdot}18H_20$	1:2:1	717.4	N/D	2 [c]	N/D	< RT	N/D	No	N/D	N/D	[46]
ChCl	urea	$NiCl_2{\cdot}6H_20$	1:2:0.1	283.5	N/D	970	1.23	< RT	215	No	31	N/D	[38]
ChCl	urea	$NiCl_2{\cdot}6H_20$	1:2:0.2	307.3	N/D	1200	1.27	< RT	215	No	120	N/D	[38]
ChCl	urea	$NiCl_2{\cdot}6H_20$	1:2:0.3	331.0	N/D	1150	1.29	< RT	215	No	130	N/D	[38]
ChCl	urea	$NiCl_2{\cdot}6H_20$	1:2:0.4	354.8	N/D	1450	1.32	< RT	215	No	133	N/D	[38]
DTAB	–	$FeCl_3$	1:0:1	470.5	$4.65\cdot10^{-5}$	N/D	1.27	32	231	No	14000 [g]	23 [g]	[19]
TTAB	–	$FeCl_3$	1:0:1	498.6	$3.84\cdot10^{-5}$	N/D	1.23	50	226	No	3000 [g]	28.98 [g]	[19]
CTAB	–	$FeCl_3$	1:0:1	526.7	$3.59\cdot10^{-5}$	N/D	1.19	62	223	No	2600 [g]	26 [g]	[19]
STAB	–	$FeCl_3$	1:0:1	474.8	$3.24\cdot10^{-5}$	N/D	1.15	72	212	No	350 [g]	30.55 [g]	[19]
TPAB	–	$FeCl_3$	2:0:1	694.7	N/D	1750	1.195	15.7	N/D	No	100	N/D	[22]
TPAB	–	$FeCl_3$	1.5:0:1	671.2	N/D	6500 [d]	1.23	38.1	N/D	No	220	N/D	[22]
ChCl	–	$ZnCl_2$	1:0:1	275.9	N/D	N/D	N/D	65	320	No	N/D	N/D	[85]
ChCl	–	$ZnCl_2$	2:0:1	415.5	N/D	$2.81\cdot10^{5}$	N/D	23	322.8	No	N/D	N/D	[85]
ChCl	–	$ZnCl_2$	3:0:1	555.1	N/D	N/D	N/D	45	328.9	No	N/D	N/D	[85]
TBPB	–	$FeCl_3$	1:0:2	663.8	N/D	1900	1.23	15.7	N/D	N/D	100 [c]	N/D	[22]
TBPB	–	$FeCl_3$	1:0:1.5	582.7	N/D	6500 [d]	1.2	38.1	N/D	N/D	210 [c]	N/D	[22]
BTPB	–	$FeCl_3$	1:0:1	501.5	N/D	N/D	N/D	57.01	N/D	N/D	N/D	N/D	[86]

(continued on next page)

Table 1 (*continued*)

HBA	HBD	Magnetic component (MC)	Molar ratio (HBA:HBD: MC)	Molecular weight, M_W [g/mol]	Magnetic susceptibility [emu·goe^{-1}]	Viscosity at 25 °C mPa·s (cP)	Density at 25 °C (g·cm^{-3})	Melting point/ freezing point [°C]	Decomposition temperature [°C]	Hydrophobicity	Conductivity at 25 °C, σ [µS/ cm]	Surface tension γ (mN m^{-1})	Ref.
BTPB	–	$FeCl_3$	1.5:0:1	671.2	N/D	N/D	N/D	52.5	N/D	N/D	N/D	N/D	[86]
BTBAB	–	$AlCl_3$	1:0:2	623.1	N/D	12.8	1.0007	< RT	129.4	N/D	16	N/D	[41]
BTBAB	–	$CuCl_2$	1:0:2	625.3	N/D	13.8	1.0039	< RT	240.3	N/D	11	N/D	[41]
BTBAB	–	$FeCl_3$	1:0:2	680.8	N/D	14.8	1.0001	< RT	310.6	N/D	22	N/D	[41]
BTBAB	–	$SnCl_3$	1:0:2	806.6	N/D	14.6	1.0043	< RT	147.5	N/D	12	N/D	[41]
BTBAB	–	$ZnCl_2$	1:0:2	629.0	N/D	13.5	1.0014	< RT	116.2	N/D	9.5	N/D	[41]
ChCl	–	$MnCl_2{\cdot}6H_2O$	1:0:1	373.5	N/D	$48^{f)}$	1.34	16.15	N/D	No	$31^{f)}$	N/D	[12]
ChCl	–	$MnCl_2{\cdot}6H_2O$	1:0:1.5	490.4	N/D	$63^{f)}$	1.348	18.35	N/D	No	$36^{f)}$	N/D	[12]
ChCl	–	$MnCl_2{\cdot}6H_2O$	1:0:2	607.3	N/D	$71^{f)}$	1.36	44.02	N/D	No	$39^{f)}$	N/D	[12]
ChCl	–	$MnCl_2{\cdot}6H_2O$	1:0:2.5	724.2	N/D	$102^{f)}$	1.372	84.15	N/D	No	$250^{f)}$	N/D	[12]
ChCl	–	$CrCl_3{\cdot}6H_2O$	1:0:2	672.3	N/D	2346	N/D	4	N/D	No	370	N/D	[87]
ChCl	–	$CoCl_3{\cdot}6H_2O$	1:0:2	408.0	N/D	392	N/D	16	N/D	No	1700	N/D	[43]
ChCl	–	$CrCl_3{\cdot}6H_2O$	2.5:0:1	615.4	N/D	N/D	1.334	< RT	N/D	No	N/D	78.0	[79]
ChCl	–	$CrCl_3{\cdot}9H_2O$	2.5:0:1	669.4	N/D	881.8	1.301	< RT	N/D	No	N/D	71.9	[39]
ChCl	–	$CrCl_3{\cdot}12H_2O$	2.5:0:1	723.4	N/D	209.9	1.287	< RT	N/D	No	N/D	69.5	[39]
ChCl	–	$CrCl_3{\cdot}15H_2O$	2.5:0:1	777.4	N/D	169.8	1.275	< RT	N/D	No	N/D	66.5	[39]
ChCl	–	$CrCl_3{\cdot}18H_2O$	2.5:0:1	831.4	N/D	57.9	1.242	< RT	N/D	No	N/D	63.8	[39]
ChCl	–	$CrCl_3{\cdot}6H_2O$	2:0:0.5	545.6	N/D	N/D	1.589	< RT	N/D	No	N/D	83.13	[40]
ChCl	–	$CrCl_3{\cdot}9H_2O$	2:0:1	669.4	N/D	223.34	1.522	< RT	N/D	No	N/D	72.84	[40]
ChCl	–	$CrCl_3{\cdot}12H_2O$	2:0:1	653.6	N/D	83.34	1.401	< RT	N/D	No	N/D	69.21	[40]
ChCl	–	$CrCl_3{\cdot}15H_2O$	2:0:1	707.6	N/D	32.10	1.363	< RT	N/D	No	N/D	66.30	[40]
ChCl		$CrCl_3{\cdot}18H_2O$	2:0:1	761.6	N/D	21.98	1.316	< RT	N/D	No	N/D	50.31	[40]
GS	–	$FeCl_3{\cdot}6H_2O$	1:0:2	879.6	$10.66{\cdot}10^{-6}$	N/D	N/D	65	N/D	N/D	N/D	37.58	[83]
–	acetamide	$MnCl_2{\cdot}4H_2O$	0:7:1	611.3	N/D	$112.8^{a)}$	N/D	< RT	193	No	$127.23^{b)}$	N/D	[53]
–	glycerol	$MnCl_2{\cdot}4H_2O$	0:3:1	474.1	N/D	$1221.25^{a)}$	N/D	< RT	146	No	$30.67^{b)}$	N/D	[53]
–	glucose	$MnCl_2{\cdot}4H_2O$	0:1:1	378.0	N/D	$434.3^{a)}$	N/D	< RT	103	No	$98.9^{b)}$	N/D	[53]
–	fructose	$MnCl_2{\cdot}4H_2O$	0:1:1	378.0	N/D	$570.4^{b)}$	N/D	< RT	108	No	$77.03^{b)}$	N/D	[53]
–	fructose	$MnCl_2{\cdot}4H_2O$	0:1:1	378.0	N/D	$6689.25^{b)}$	N/D	< RT	103	No	$6.82^{b)}$	N/D	[53]

N/D – no data available; M_W - Molecular weight [g/mol] which has been determined using the following equation: $M_W = x_{HBA}{\cdot}M_{HBA} + x_{HBD}{\cdot}M_{HBD} + x_{MC}{\cdot}M_{MC}$, where: x_{HBA} - the number of HBA moles in the MDES structure [-]; x_{HBD} - the number of HBD moles in the MDES structure [-]; x_{MC} - the number of MC moles in the MDES structure [-]; M_{HBA} - molar mass of HBA [g/mol]; M_{HBD} - molar mass of HBD [g/mol]; M_{MC} - molar mass of MC [g/mol]; [a)] Measurements at 21 °C; [b)] Measurements at 29 °C; [c)] Measurements at 30 °C; [d)] Measurements at 40 °C; [e)] Measurements at 65 °C; [f)] Measurements at 70 °C; [g)] 30 mM solution of MDES in water;

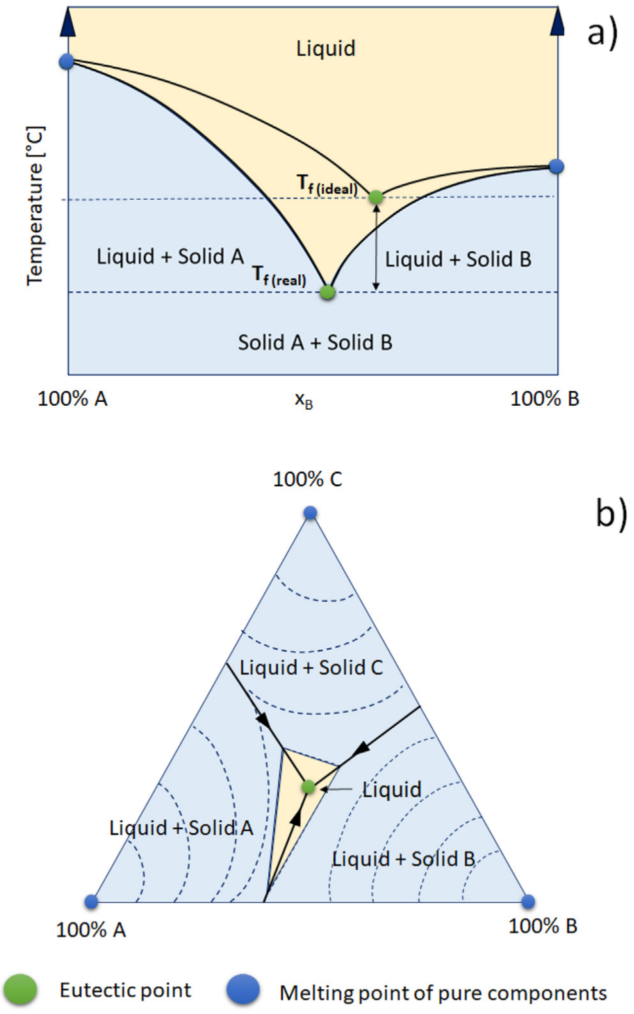


Fig. 4. **a)** Binary and b) ternary phase diagram for eutectic mixtures.

density depend on the components used for MDES synthesis and their molar ratio. It can be observed the component that has the greatest impact on the density of MDES is HBA (or HBD in two-component MDES), because it causes the formation of the so-called "gaps" in MDES structures which contribute to the increase in DES density. The magnetic component influences the density changes to a much lesser extent due to the simpler structure [41]. Theoretically, the use of hydrated MC should significantly reduce the density. However, a relatively small addition of water only slightly reduces this parameter. Probably much more water should be used to significantly affect the solvent density [39,40]. In separation techniques, i.e. extraction, the addition of water can increase the difference between the densities of the phases, ensuring easier and faster separation. However, such modification is limited to hydrophilic MDES. The temperature also has a significant influence on the MDES density values. The decrease in temperature of MDES affects a decrease in the kinetic energy of the molecules, which causes a density increase. This is due to the fact that at low temperatures the decrease in the movement of the MDES molecules and a consequent decrease in the molar volume of the eutectic complexes can be observed [42,43]. However, many industrial processes require temperatures close to room temperature. It is related to the economics of the processes. Moreover, in extraction processes, a change in the temperature of the solvent also changes the temperature of the second phase, i.e. it does not improve the phase separation.

3.4. Viscosity

Viscosity is a crucial parameter in many applications of MDES. The low viscosity of MDES makes solvents easy to handle and decreases energy costs. However, conventional DES and MDES are characterized by high viscosity (greater than100 cP) [1,2,18]. The exact viscosity of the eutectic liquids depends mainly on the nature of components used in their preparation (i.e. HBA, HBD, MC), molar ratios, as well as the strength and type of interactions between the components. The viscosity of MDES in most cases is higher than that of conventional deep eutectic solvents. Viscosity of ternary MDES i.e. TOAB: decanoic acid:$CoCl_2$ (1:2:0.5) and TOAB: decanoic acid:$MnCl_2$ (1:2:1) are respectively 286400 and 29150 cP at room temperature [4]. While the viscosity of TOAB: decanoic acid (1:2) is 472.6 cP, which is 61 and 605 times lower than the MDES, respectively [33].

The high viscosity of MDES is caused, among others, by: (1) Presence of very strong hydrogen bonds between HBA and HBD which cause lower mobility of free species within the eutectic molecule; (2) Large ion sizes in HBA structure and small empty volumes. It is a so-called steric effect which can be quantified by the hole theory [44]; (3) The occurrence of relatively strong electrostatic and van der Waals interactions between HBA, HBD and MC; (4) The length of the alkyl chain of HBA or HBD. The longer the chain, the higher the MDES viscosity; (5) High content of the magnetic substance in the structure of DES, leads to the enhancement of the van der Waals interactions between MC and HBA and HBD molecules. In addition, an increase in the content of MC in the MDES structure may lead to the formation of the so-called bridges connecting MC to other groups of molecules. As the MC content increases, the number of bridges increases and forms a network between the different active groups of MDES, and consequently contributes to an increase in viscosity [45]; (6) The addition of water to eutectic structures with anhydrous magnetic salts usually leads to a decrease in dynamic viscosity. It is noticeable in MDES structures i.e. ChCl:ethylene glycol:$NiCl_2{\cdot}xH_2O$ (1:2:1), ChCl:$CrCl_3{\cdot}xH_2O$ (2.5:1), and ChCl:$CrCl_3{\cdot}xH_2O$ (2:1) where × increase from 6 to 18. For those MDES viscosity decrease from 96.8 to 2.0 cP at 30 °C, from 881.8 to 57.9 (at 30 °C), and from 223.3 to 22 cP (at 25 °C), respectively [39,40,46] The decrease in viscosity can be explained by the lower viscosity of water in comparison to DES. In addition, the viscosity of MDES diminishes greatly with increasing temperatures, which can be described by Arrhenius or Vogel-Fulcher-Tammann model. This is due to the fact that an increase in temperature cause an increase in the average speed of the selected MDES components in the liquid phase, which decreases the intermolecular forces. This can reduce the fluid resistance to flow and change the viscosity [47].

3.5. Magnetic properties

The greatest difference between conventional DES and MDES is the paramagnetic properties of the solvents, under the application of an external magnetic. This property is particularly important in extraction, microextraction, manipulation within microfluidic devices, and magnet-based sensor processes [6]. High magnetic moments of MDES accelerate and simplify the after mentioned processes, as there is no need for a tedious centrifugation step. Moreover, MDES can be isolated easily from the sample solution through the use of a magnetic field [20]. It should be mentioned that MDES does not retain any magnetization properties without an externally applied magnetic field, because thermal motion causes the spins to become randomly oriented without it, as measured by a superconducting quantum interference device magnetometer [47]. The paramagnetic properties are influenced by the selection of the appropriate MC component, as well as its molar ratio in the MDES structure. The higher the degree of magnetization of pure MC salts, the better magnetic properties of MDES can be expected. The dependence of popular magnetic components can be observed according to decreasing magnetic susceptibility $GdCl_3 > FeCl_3 > MnCl_2 > CoCl_2 > CrCl_3 > NiCl_2 > MgCl_2 > ZnCl_2$. Theoretically to obtain the best MDES properties, $GdCl_3$ should be used as the main component in MDES structure. However, to date, no MDES have been prepared with a melting point below RT. Among MDES, the most popular components of MC are $FeCl_3$ and $MnCl_2$ due to their high availability, low price, low melting point compared to other paramagnetic salts, as well as relatively good magnetic susceptibility. However, so far only a few MDES have been tested for paramagnetic properties. The magnetic susceptibility of MDES are $3.81\cdot10^{-5}$, $2.65\cdot10^{-5}$, $2.14\cdot10^{-5}$, $1.31\cdot10^{-5}$, $0.0546\cdot10^{-5}$, $0.0514\cdot10^{-5}$, and $0.0165\cdot10^{-5}$ $emu\cdot goe^{-1}$ for TOAB: decanoic acid: $MnCl_2$ (1:2:1), lauric acid: decanoic acid:$MnCl_2$ (1:2:0.5), lauric acid: decanoic acid:$CoCl_2$ (1:2:0.8), TOAB:decanoic acid:$CoCl_2$ (1:2:0.5), ChCl:phenol:$FeCl_3$ (1:2:1), ChCl: ethylene glycol:$FeCl_3$ (1:4:1), and ChCl:p-cresol:$FeCl_3$ (1:3:1), respectively [4,17,20]. On the basis of the obtained results, it can be observed that MDES with $MnCl_2$ are characterized by the highest magnetic susceptibility. Slightly lower values can be observed for MDES consisting of $CoCl_2$. In addition, it can be observed that the higher the MC content and the higher the magnetic moment of MC, the better the paramagnetic parameters of MDES are. However, due to insufficient available data, it is difficult to determine the effect of the remaining components of MDES on increasing or decreasing magnetic susceptibility.

3.6. Hydrophobicity / hydrophilicity

According to the definition, hydrophobic substances do not have an affinity to water, and tend to repel or not absorb it. Solvents which are able to absorb more than 0.2 wt% of water are considered hydrophilic substances [11]. Most of the MDES are hydrophilic due to the strong hygroscopic nature of magnetic component. Due to the necessity to obtain paramagnetic properties, the MC content in the MDES structure must be high and, thus it is very difficult to obtain MDES that are hydrophobic in nature. Nevertheless, hydrophobicity is a key parameter that allows, among others, extraction of substances from water samples. In the literature there are only a few examples of such substances, including TOAB:decanoic acid:$MnCl_2$ (1:2:1), TOAB: decanoic acid:$CoCl_2$ (1:2:0.5) [4], Lauric acid:decanoic acid:$MnCl_2$ (1:2:0.5), and Lauric acid:decanoic acid, $CoCl_2$ (1:2:0.8) [17], and ChCl:p-cresol:$FeCl_3$ (1:3:1) [20]. In one of the published studies, the hydrophobic character of MDES was proved by a simple test that measures the water content of the MDES before and after mixing with water. The concentration of water in MDES before tests was $1.205\cdot10^4$ ppm and $0.913\cdot10^4$ ppm for TOAB: decanoic acid:$MnCl_2$ (1:2:1), TOAB:decanoic acid:$CoCl_2$ (1:2:0.5), respectively. After water addition, the concentration of water in MDES increased slightly to $2.097\cdot10^4$ and $1.914\cdot10^4$ ppm, respectively [4]. For the remaining MDES, i.e. lauric acid: decanoic acid: $MnCl_2$ (1:2:0.5), and lauric acid: decanoic acid:$CoCl_2$ (1:2:0.8), and ChCl:p-cresol: $FeCl_3$ (1:3:1) only visual tests were performed to confirm their hydrophobicity. Nevertheless, the results indicate that the use of highly hydrophobic HBA and HBD is necessary to obtain a hydrophobic MDES.

3.7. Ionic conductivity

Ionic conductivity is a very important parameter in many electrochemical applications [48]. This parameter strongly depends on the mobility of the ions, which is associated with dynamic viscosity and the number of charge carriers [49]. Theoretically, ion association can cause a reduction in ionic conductivity due to the decrease of the number of available diffusible ions. Therefore, MDES with few ion-ion interactions and delocalized charges should show high conductivities. In addition, the ionic conductivity of MDES with quaternary ammonium and phosphonium salts decrease as the alkyl chain length increases [49–51]. This is due to the fact that longer alkyl chains cause higher hydrophobicity of MDES [19]. On the basis of the data compiled in Table 1, it can be concluded that the conductivity is influenced by both, the type of HBD and the type of MC and their molar ratios in MDES structures. However, it is closely related to the MDES dynamic viscosity. It can be noted that the ionic conductivity decreases with the increase of viscosity, due to the fact that high viscosity prevents the movement of ions. The ionic conductivity of three components MDES composed of choline chloride, $MgCl_2$, and different HBD is in the range from 2090 to 9100 μS/cm, which is comparable with conventional DES [1,11,45,52]. The ionic conductivity of quaternary ammonium salts and $FeCl_3$ in various molar ratios, as well as MDES, contain hydrated magnetic component ale lower (6.82 – 220 μS/cm) and they are comparable to aqueous systems [22,38,53]. In addition, high temperatures can reduce the viscosity and increase the ionic conductivity of MDES, which is in line with the standard behavior of liquids [54].

3.8. Surface tension

Surface tension is the parameter that measures cohesive forces and the intensity of interactions between components in the mixture at the surface. According to the definition, the surface tension is the energy required to increase the unit area of a new surface or as the force to close unit length in the surface of a liquid. This parameter is of great importance in separation processes i.e. distillation, absorption, extraction, and microextraction [55–57]. However, only few papers provide MDES surface tension data. Based on the previous studies on ionic liquids and conventional DES it can be concluded that many factors can influence the surface tension of MDES i.e. temperature, type of HBA, HBD, MC, and their amounts in the DES structures [55–57]. The surface tension of conventional DES and ionic liquids are typically in the range from 40 to 65 $mN\cdot m^{-1}$ at 25 °C [55,58]. On the other hand, the values of MDES are within this range of 23 – 83.1 $mN\cdot m^{-1}$, which shows a much wider range of surface tension of individual MDES, which depends on the type of substances used for their synthesis [11,39,40]. The lowest surface tension values are observed for DTAB:$FeCl_3$ (1:1), TTAB:$FeCl_3$ (1:1), CTAB: $FeCl_3$ (1:1), and STAB: $FeCl_3$ (1:1), which are 23, 29, 26, and 31 $mN\cdot m^{-1}$, respectively [19]. The low surface tension of MDES is probably caused by long alkyl chains in the ammonium quaternary salts in MDES structures, which decreased charge density, thus decreasing the importance of electrostatic interactions between MDES components. The surface tension of MDES decrease with an increase in temperature, which shows the typical behavior of liquids [59].

3.9. Critical evaluation of MDES properties

Compared to conventional organic solvents and DES, MDES have several advantages and limitations. The greatest advantage of MDES is their paramagnetic property, which is very useful in the case of separation processes as extraction or microextraction. This allows easier phase separation through a magnetic field without a tedious centrifugation step. However, the paramagnetic property of MDES is relatively low. Therefore, it is necessary to use strong neodymium magnets, rather than the popular, cheap ferrite magnets. Very often even the use of strong magnets may not be enough to separate the phases. To obtain enough paramagnetic properties, the content of the magnetic component in the MDES structure must be high. The increase in MC content significantly affects other physicochemical parameters compared to conventional DES. The first property that determines the further usefulness of MDES is their melting/freezing point. Based on a literature review, there are a very limited number of MDES that are liquids at room temperature. This is a major drawback of MDES due to the fact that many processes, both analytical and industrial, require the application of solvents that are liquid at 20 °C. The drop in the melting/freezing point of MDES compared to pure substances is slight. Therefore, according to the previous work, it can be assumed that we are rather dealing with simple eutectic mixtures than deep eutectic solvents [60]. This is likely due to the formation of weaker electrostatic interactions between MDES components rather than strong hydrogen bonds. Consequently, this may cause MDES structures to break down in contact with primary solvent i.e., water in the extraction process, which will form competing stronger H-bonds with the individual components. This significantly limits the usefulness of MDES. However, the mechanisms of MDES formation are still poorly understood. Therefore, more detailed studies should be conducted to confirm these assumptions.

The relatively high MC content in the MDES structures can reduce solvent hydrophobicity. This is due to the hydrophilic nature of common MCs. The solubility of $FeCl_3$, $GdCl_3$, $CoCl_2$ and $MnCl_2$ in water varies from 436 to 946.5 g/L. Therefore, it is difficult to obtain MDES that are stable in aqueous solutions and do not tend to dissolve in water. This affects the problems of the selection of appropriate solvent for the extraction of substances from aqueous samples. The presence of a magnetic component in MDES structures also affects other basic rheological properties, including density and dynamic viscosity. Both of them can accelerate and simplify the extraction processes. To obtain a good phase separation in extraction processes, the densities of the primary solvent and MDES should be significantly different. However, so far known hydrophobic MDES have a similar density to water, which significantly limits their usefulness in extraction processes. Hydrophilic MDESs show a much greater diversity in density values, which can be tuned by selecting the appropriate HBA, HBD, and MC depending on the type of sample matrix.

The dynamic viscosity of MDES is higher compared to conventional organic solvents. In most applications, such a high viscosity will negatively affect the mass transfer processes. Nevertheless, there are several studies in which it has been proved that higher viscosity has a positive effect on phase separation in the extraction process [61]. Moreover, when using MDES as impregnating substances, one should aim for the highest possible viscosity to permanently deposit the MDES on the surface of the adsorbent [62,63]. Therefore, the choice of MDES should be dictated by the end-use.

From an economical point of view, the thermal decomposition temperature of MDES is an important parameter due to the fact that in many processes, solvents are regenerated at high temperatures. Whereas, regeneration is carried out to remove impurities from solvents and reuse them. Therefore, the decomposition temperature should be as high as possible to avoid weakening or decaying the interactions between HBA, HBD, and MC, which can lead to changes in physicochemical properties. Fortunately, the published data show that MDESs are characterized by higher thermal decomposition temperatures than conventional organic solvents and DES, which potentially increases the range of the MDES application. In addition, MDES are characterized by a wide range of surface tension, which can also increase the scope of application.

There are some serious limitations of MDES compared to conventional DES. Despite the similar procedures for the preparation of eutectic mixtures, the synthesis of DES is much simpler and shorter than that of MDES. In order to obtain DES, it is usually sufficient to mix the ingredients for a few minutes at an elevated temperature (about 80–90 °C). In contrast, to obtain MDES, the mixing process must be much longer and may take up to several hours.

From the point of view of green chemistry and green engineering, it is important to use only non-toxic and biodegradable solvents. However, no toxicity and biodegradability studies have yet been established with MDES. When considering the application of MDES as solvents in industrial processes, they should also be non-corrosive. However, it can be assumed that MDES will be characterized by its ability to corrode most of the metals due to the high content of highly corrosive MC in MDES the structures [64–66]. Nevertheless, more research needs to be done to prove these assumptions.

All these advantages and disadvantages of MDES in comparison to conventional DES, are presented in Fig. 5.

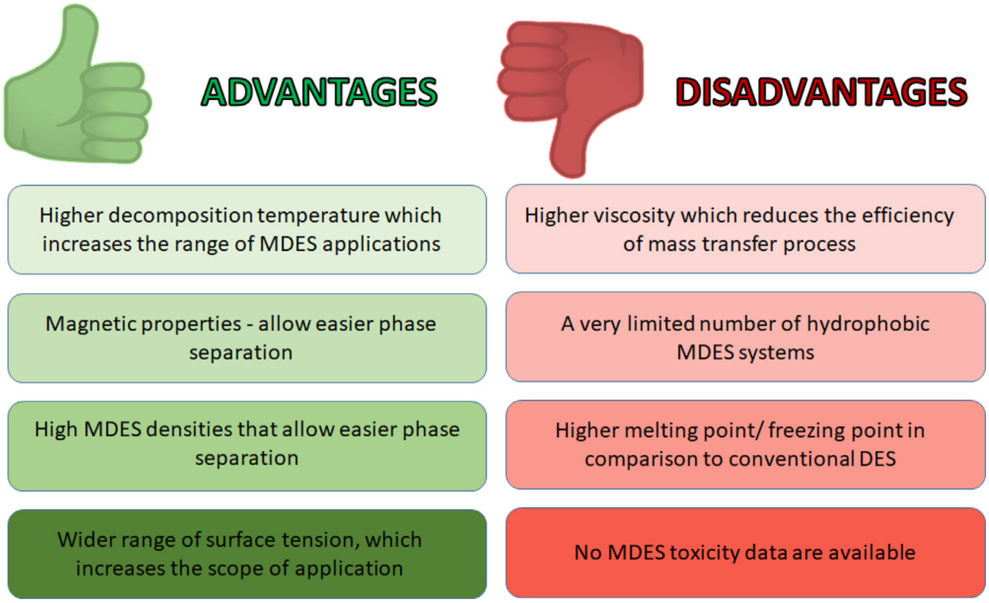


Fig. 5. Comparison of the pros and cons of MDES to conventional DES.

4. MDES applications

An overview of all MDES presented so far in the literature is shown in Table 2. As can be seen, by choosing proper components, it will be possible to apply MDES for many uses in laboratory research as well as potentially as sustainable solvents in industry. All the applications are further discussed in the below sections. Presented applications are categorized in two sections, as a media for analytical microextraction, and as solvents in the synthesis of catalysts.

4.1. Extraction processes

Ferrofluids based on MDES are uniform solid–liquid composite material containing magnetic nanoparticles suspended in a (hydrophobic) DES. During extraction, they are stable in solution and mostly their densities are lower than water. After extraction, the extracting ferrofluid can be easily separated from the aqueous solution by an external magnet. The first application of ferrofluid in liquid phase microextraction (LPME) was reported in 2010 by Lee group [67]. They used a ferrofluid which was composed of silica-coated magnetic particles and 1-octanol as the extractant solvent for the extraction of sixteen polycyclic aromatic hydrocarbons as model compounds from river water. However, using DESs as emerging green solvents for this purpose is new. The first report in this area was probably a work by Khezli and Daneshfar which was published in 2017 [10]. The authors described the importance on using magnetic DESs as: "In our previous reported method, ultrasound-assisted liquid–liquid microextraction based DES (UALLME-DES) was used to extract of three phenolic acids. Although UALLME-DES has excellent extraction efficiency, the separation of dispersed microdroplets of DESs created by the ultrasonication of sample solution was difficult and needs centrifuge instrument. Therefore, in this study, to overcome the shortcoming of UALLME-DES method, two novel hydrophilic MDESs were prepared". This sentence clearly shows the main advantage of microextraction by using magnetic DESs in comparison to DESs. They prepared two MDES as ChCl:phenol:$FeCl_4$ and ChCl: ethylene glycol:$FeCl_4$. After full characterization, MDES were applied in UALLME of thiophene in *n*-heptane as a model analyte. Initial results indicated that ChCl:phenol:$FeCl_4$ has higher extraction efficiency than ChCl: ethylene glycol:$FeCl_4$. MDES was obtained simply by mixing the ChCl with EG and anhydrous $FeCl_3$ at a molar ratio of ChCl:ethylene glycol:$FeCl_3$ of 1:4:1 at 80 °C until a homogeneous clear liquid was formed. For performing microextraction, 1.5 mL of *n*-heptane containing thiophene and 20 μL of MDES were put in a vial placed inside an ultrasound water bath for 5 min. After that, the fine dispersed droplets of MDES were collected by putting a magnetic rod (B = 0.66 T) in the sample solution until *n*-heptane phase was cleared. Finally, ~1 μL of *n*-heptane phase was injected into the GC for analysis. Another advantage of using MDESs in comparison to magnetic ionic liquids is "MDES can be prepared more cheaply (from common reagents) and easily (by simple complexion of the salt with the hydrogen bond donor). Moreover, the synthesis of magnetic ionic liquids is a time-consuming process but MDES can be successfully prepared with high purity in a short time", as the authors of the article explain.

One year later, hydrophobic deep eutectic solvents were prepared and combined with magnetic clay to form a ferrofluid and used for direct microextraction of 11 explosive residues including 2-nitrotoluene, 3-nitrotoluene, 1,2-dinitrobenzene, 1,3,5-trinitrobenzene, 2,6-dinitrotoluene, cyclotetramethylene tetranitramine, cyclotrimethylenetrinitramine, hexanitrohexaazaisowurtzitane, tetryl, and pentaerythritol tetranitrate, and 2,4-dinitrotoluene in soil and water samples [68]. To synthesize hydrophobic DESs, decanoic, caprylic, oleic, lauric, valeric, propionic, lactic, butyric, acrylic, acetic, stearic, palmitic, glutamic, succinic, tartaric, malonic, or oxalic acid were mixed with DL-menthol as HBA in different molar ratios before addition of 50 mg of magnetic montmorillonite clay/Fe_3O_4 nanocomposite (nanoclay) to 1 mL of them. It was found that the obtained ferrofluid ponded a stable and uniform solid–liquid composition. To perform extraction, 50 μL of this ferrofluid was placed in a 15 mL vial containing 10 mL sample and stirred firmly for 30 min and after extraction, the micro-drop was removed with a rod magnet and dissolved in 500 μL of acetonitrile and sonicated for 4 min to desorb explosives. Finally, 50 μL of the resulting solution were injected into a HPLC. Limits of detection values were in the range of 0.22–0.91 μg/L, the enrichment factors varied between 23 and 93 and the relative standard deviations and recoveries were < 10 % and between 88 and 104 %, respectively. This research indicates the potential use of hydrophobic magnetic ferrofluid as a green solvent for enhancing the extraction of emerging materials from water and soil samples.

For the first time, Liu et al [69] used a DES as function monomers in molecular imprinted technology. MDES was prepared and adopted as functional monomer in a molecularly imprinted polymer (MIP) for the selective recognition and separation of Bovine hemoglobin. The obtained MIPMDES could separate proteins rapidly by an external magnetic field. They used it to separate template protein from the mixture of proteins and real samples. Additionally, compared to other magnetic MIPs, such as dopamine and acrylamide, the MIPMDES presented an enhanced adsorption capacity and imprinting factor to proteins. Meanwhile, the synthesis of DES function monomer was simple. Adsorption capacity of magnetic MIPMDES was found to be 169.32 mg g^{-1}, which was almost four times higher than that of magnetic non-imprinted polymer, prepared in the same way as MIPMDESs. Isotherms were in accordance with Langmuir model. After three adsorption/elution cycles, the adsorption capacity was only about 7.93 % less.

In a paper published in 2020, Xia and colleagues reported the application of a combined MIPMDES composed of a ternary DES to selectively extract baicalein from the *Scutellaria baicalensis* Georgi [70]. The ternary DES was prepared with ChCl, oxalic acid and 1,2-propanediol, and Fe_3O_4 particles were selected as the magnetic cores for preparation of MIPMDES. The system was characterized through morphology, core–shell structure, particle size, chemical bonds, weight ratio of modified layer, magnetic property and specific surface area. Moreover, binding experiments and selectivity test of MIPMDES were discussed. After extraction, quantitation of the analyte was performed by HPLC. Extraction was performed simply in batch mode, i.e. 20 mg of MIPMDES was added to 1.5 mL extract solution sample and the mixture shaken at 120 rpm for 60 min at 35 °C in a vibrator. MIPMDES was collected by a magnet. This adsorbent could be used for at least six extraction cycles, but its adsorption capacity was decreased slightly after that. The method was a linear range of 0.500–179 μg mL^{-1}, LOD of 0.0387 μg mL^{-1}, LOQ of 0.129 μg mL^{-1}; with an intra-day RSD 1.43 % and Inter-day RSD 1.61 %. A high selectivity toward baicalein extractants permitted enriching it efficiently from real samples, being followed the pseudo-second-order model for adsorption kinetics of this compound.

MIPMDES was also used to separate transferrin from human serum [71]. For its preparation, 30 mg of previously prepared Fe_3O_4 were sonicated in 10 mL phosphate buffer (20 mM, pH = 5.0). Then, 1 mg of transferrin, 11 mg of N,*N*-methylenebisacrylamide and 50 μL of ChCl and acrylic acid (molar ratio of 1:2) DES were added to the mixture and shake for 1 h to proceed pre-polymerization. Tetramethylethylenediamine (20 % aqueous solution, 70 μL) were added to the system to initiate the polymerization. The system was polymerized in dark for 24 h at

Table 2
Applications of MDES-based microextraction techniques.

Analyte/sample	Microextraction method	DES components	Magnetic part	Ref
Drugs				
Thiophene in *n*-heptane	Ultrasound-assisted liquid–liquid microextraction	Choline chloride/phenol and choline chloride/ethylene glycol	$FeCl_4$	[10]
Mefenamic acid in human urine	Vortex assisted liquid microextraction	Acetic acid with DL-Menthol	Oleic acid coated Fe_3O_4 nanoparticles	[76]
Meloxicam in human blood plasma and urine	Ferrofluid was quickly injected into the sample solution using a glass syringe	Choline chloride and ethylene glycol	Silica-coated Fe_3O_4 nanoparticles	[78]
Warfarin in plasma and urine samples	Ferrofluid was quickly injected into the sample solution using a syringe	Tetramethylammonium chloride and thymol	Magnetic-activated charcoal	[80]
Doxycycline in urine, blood plasma and milk	Synthesized ferrofluid was used in a vortex-assisted dispersive liquid–liquid microextraction	Octanoic acid and DL-menthol	Fe_3O_4 magnetic nanoparticles	[81]
Herbicides and pesticides				
16 pesticides in sea, river, spring, agricultural, and underground water	Polymeric hydrogel	Acrylic acid-menthol	Fe_3O_4 in the structure of DES	[72]
Triazine herbicides in rice and maize	Vortex assisted dispersive liquid–liquid extraction	Tetrabutylammonium chloride/ ethylene glycol	$FeCl_4$ in the structure of DES	[23]
Protein and DNA				
Bovine hemoglobin in calf blood	MDES was used as molecularly imprinted polymer for batch extraction	Choline chloride and methacrylic acid (molar ratio 1:2)	Fe_3O_4 in the structure of DES	[69]
Plasmid DNA from a bacterial cell lysate	Liquid-liquid microextraction	Decanoic acid and tetraoctylammonium bromide mixed by different metal chlorides	$FeCl_3$, $MnCl_2$, $CoCl_2$ and $GdCl_3$ metal chlorides	[4]
Plasmid DNA from a bacterial cell lysate	Vortex assisted liquid microextraction	Decanoic acid and lauric acid mixed by different metal chlorides	$FeCl_3$, $MnCl_2$, $CoCl_2$ and $GdCl_3$ metal chlorides	[17]
Transferrin in human serum	Ultrasound-assisted dispersive solid liquid microextraction	Choline chloride and acrylic acid	Fe_3O_4	[71]
Explosives				
11 explosive residues in soil and water	Liquid-liquid microextraction in a vial	A long list of fatty acids in combination with DL-menthol	Magnetic montmorillonite clay/Fe_3O_4 nanocomposite	[68]
Polycyclic aromatic hydrocarbons				
16 polycyclic aromatic hydrocarbons in saliva and urine samples	Air-assisted liquid–liquid microextraction	Choline chloride and stearic acid	toner powder was used as magnetic particles and was acted as DE support in the preparation of ferrofluid	[67]
16 polycyclic aromatic hydrocarbons in grilled meats	Ultrasonic assisted liquid microextraction	Menthol and decanoic acid	Fe_3O_4 nanoparticles coated with tetraethoxy silane	[74]
31 polycyclic aromatic hydrocarbons in grilled meats	Magnetic dispersive micro solid phase extraction–dispersive liquid–liquid microextraction	Choline chloride and decanoic acid	Fe nanoparticles	[75]
Foodstuff				
Morin in apple and grape juices, extract of onion and green tea infusion	Ultrasonic assisted micro-solid phase extraction	Tetramethylammonium chloride/ ethylene glycol	$SiO_2@Fe_3O_4$ nanoparticles	[79]
Naringenin, gallic acid and hesperetin in orange, red grape and sour cherry juices	Ultrasonic assisted micro-solid phase extraction	Choline chloride-Ethylene glycol, tetramethylammonium chloride-ethylene glycol, and tetraethylammonium chloride-ethylene glycol	Fe_3O_4 with adipic acid	[80]
Hexanal and heptanal in edible oils	Ultrasonic assisted liquid–liquid microextraction	Choline chloride/*para*-cresol	$FeCl_4$	[20]
Chiral mefentrifluconazole in cereal	Dispersive liquid–liquid microextraction	Octyltrimethylammonium bromide, cobalt chloride, acetic acid	$CoCl_2$	[82]
Cation				
Cobalt in tap water, bottled, mineral water, seawater, and river water	Ultrasonic assisted dispersive liquid phase microextraction	Menthol/decanoic acid	Fe_3O_4 modified with sodium dodecyl benzene sulfonate	[77]
Plants extracts				
Baicalein from *Scutellaria baicalensis* Georgi	Batch extraction with solid MIP-MDES	Choline chloride, oxalic acid and 1,2-propanediol	Fe_3O_4 nanoparticles	[70]
Catalyst production				
Industrial use of MDE in production of a catalyst	This catalyst was used for high yielding benzoin condensation and the efficient synthesis of pyrrole derivatives. It could be reused at least 4 times	Magnetic gemini-surfactant-based deep eutectic from a synthetic gemini-surfactant and FeCl3··6H2O	gemini-surfactant 1,3 bis (dodecyldimethylammonio) 2 hydroxypropane dichloride	[83]
Industrial use of MDE in production of a catalyst	This catalyst was used for the synthesis of substituted tetrahydropyrazolopyridines and pyrroles under very mild conditions	1:4 mol ratio of $CoCl_2$:choline chloride	$CoCl_4^{2-}$	[84]

25 °C. Finally, the prepared MIP-MDES eluted by 2 % sodium dodecyl sulphate and 2 % acetic acid for removing template molecules. In this synthesis, DES acted as the functional monomer and N,*N*-methylenebisacrylamide as the crosslinker in the polymerization, Tetramethylethylenediamine as the initiator, and acrylic acid functionalized Fe_3O_4 as a donor of magnetic properties and the material matrix. For separation and detection of transferrin, 4 mg of MIP-MDES were ultrasonically dispersed in 1 mL of the protein solution, shaking for 1 h. After adsorption, a magnet was used to separate MIP-MDES from the solution and the supernatant was measured by Coomassie blue-ultraviolet detection method. Then, sodium dodecyl sulphate–polyacrylamide gel electrophoresis was used to further verify the selective adsorption and the competitive adsorption experiment. Prepared MIP-MDES could be reused for at least 6 times. This adsorbent showed a fast adsorption for transferrin due to the existing electrostatic adsorption and low template molecule usage.

A MIP-MDES polymeric hydrogel was prepared through a thermal frontal polymerization in 4 min, using acrylic acid-menthol DES (as a functional monomer), ammoniumpersulfate (as initiator), and acrylic acid-Fe_3O_4 nanoparticles as cross-linker [72]. The hydrogel was utilized as a sorbent in magnetic solid-phase microextraction of 16 pesticides coupled with GC–μECD for their determination. The LODs were in the range of 0.002–0.120 $\mu g\ L^{-1}$, and the linear range was between 0.003 and 20 $\mu g\ L^{-1}$. RSDs were in the ranges of 0.8–6.8 % and enrichment factors were from 152 to 550.

A new ferrofluid prepared from toner powder and DES was used in air-assisted liquid–liquid microextraction procedure for extraction of sixteen polycyclic aromatic hydrocarbons (i.e., anthracene, acenaphthene, benzo[*a*]anthracene, acenaphthylene, benzo[*b*]fluoranthene, benzo [ghi]perylene, fluorene, benzo[*k*]fluoranthene, indeno[1,2,3-cd] pyrene, chrysene, benzo[*a*]pyrene, fluoranthene, naphthalene, dibenzo [a,h]anthracene, phenanthrene, and pyrene) from urine and saliva samples of tobacco smokers by Jouyban, et al [73]. In this work, a hydrophobic DES was prepared by mixing ChCl and stearic acid under mild conditions and used as a support solvent in the preparation of ferrofluid from toner powder. Then, a few microliters of the prepared ferrofluid was mixed with the sample by performing aspirating/dispersing cycles. To collect the ferrofluid, a magnet was placed at the outside of the tube and the solution was discarded. The analytes in the collected phase were back-extracted into *n*-heptane and determined by GC/MS. LOD in the range of 18–63 ng/L in saliva and urine samples. Extraction recoveries and enrichment factors ranged from 61 to 84 % and 305 to 420, respectively. Aliquat 336 was used as the surfactant to prevent particles from agglomeration.

In another paper [74], Jouyban, et al. reported the use of a ferrofluid prepared from Fe_3O_4 nanoparticles coated with Tetraethoxy silane mixed with menthol and decanoic acid DES. By using ultrasound assisted liquid microextraction, they could preconcentrate the same 16 polycyclic aromatic hydrocarbons using this ferrofluid. Analytes were back extracted to *n*-hexane before GC/MS analysis.

Polycyclic aromatic hydrocarbons were also determined in five mascara samples using deep eutectic solvent-coated magnetic nanoparticles for magnetic dispersive micro solid phase extraction–dispersive liquid–liquid microextraction of them [75]. Deep eutectic solvent coated magnetic nanoparticles were synthesized sonochemically and fully characterized. For the preparation of the sorbent, 5 mL of ChCl:decanoic acid DES was mixed with 1.0 mL dimethylformamide and $Fe(CO)_5$ was added and sonicated at 60 ℃ for 3 h at a power of 100 w. Color change of solution from bright–orange to black was considered as the end of the reaction. The obtained nanoparticles were magnetically separated and used for the extraction. Microextraction was a multi-step procedure as follows. First, analytes were extracted from mascara into an aqueous solution composed of methanol and deionized water (30:70, v: v), then the sorbent was added into the solution and the mixture was vortexed. After that, the sorbent was separated from the aqueous solution and the analytes were desorbed by methanol with the aid of vortexing. The entire elution solvent was collected and mixed with CCl_4 and dispersed into NaCl solution. Their method was validated and LOD and LOQ within the ranges of 0.33–0.57 and 1.1–1.9 ng g^{-1}, respectively; with RSD values $\leq$ 8.6 %. Adsorbent could be used for 3 times with an extraction recovery between 80 and 95 %. Enrichment factors were not reported.

In a key paper [4], Ding's group discussed synthesis of four hydrophobic magnetic deep eutectic solvents and their application in DNA separation. Four hydrophobic DES based on HBD decanoic acid and HBA tetraoctylammonium bromide were prepared and mixed with different metal chlorides ($FeCl_3$, $MnCl_2$, $CoCl_2$ and $GdCl_3$), to prepare hydrophobic MDES for the extraction of DNA from a bacterial cell lysate. These MDES compared to traditional DES, can be easily separated and collected through application of an external magnetic field, allowing fast extraction process without tedious and time-consuming centrifugation steps. They also showed the possibility of synthesizing hydrophobic MDES with adjustable physical and chemical properties. By changing the molar ratio and cation of mixed metal chloride, hydrophobic MDESs with certain magnetism could be obtained. The hydrophobicity of DES allows separation and purification of samples in aqueous environment (see Fig. 6). The developed hydrophobic MDES-based extraction procedure performed rapid and highly efficient extraction of nucleic acid from a matrix containing metal ions or

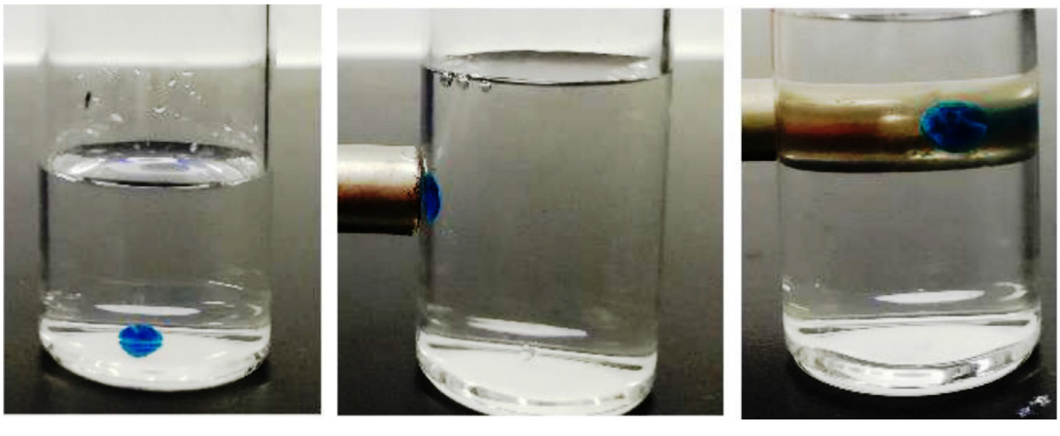


Fig. 6. After performing extraction, hydrophobic MDES can be quickly collected by an external magnet (from ref [4], with permission).

proteins. It could also extract plasmid DNA from bacterial cell lysate to obtain a high-quality template for polymerase chain reaction. Only 25.0 μL of hydrophobic MDES were used to extract different DNA from a 1.0 mL solution. The instrument used for this purpose was a simple spectrophotometer which has its own merits of simplicity and cheapness.

The same group at the same year [17] reported a very similar work for the extraction of DNA from bacterial cell lysate again by using hydrophobic MDES. They prepared a series of four low-viscosity hydrophobic MDES by mixing decanoic acid and lauric acid with metal ion chloride which was used in their previous work. Synthesis was simulated by density functional theory calculation. Prepared hydrophobic MDESs again were used for the extraction of DNA. Interaction and corresponding binding sites between hydrophobic MDESs and DNA were investigated by FT-IR and density functional theory calculation. Interactions between DNA and the hydrophobic MDES are shown in Fig. 7. This time, a vortex extraction method was applied for selective extraction of DNA. This technique could extract the analyte from a complicated matrix in only 5 s. For a 1.0 mL sample solution volume, containing 1000.0 nM DNA; by using 20.0 μL volume of hydrophobic MDES, extraction efficiency better than 77 % was achieved.

In another report of using hydrophobic MDES as ferrofluid for LPME, Fe_3O_4 nanoparticles combined with hydrophobic DES was prepared and coupled with vortex-assisted LPME, to preconcentrate and determine mefenamic acid in urine samples, following HPLC [76]. The effect of parameters affecting microextraction, as pH, ferrofluid volume, ionic strong of the sample solution and vortex time were optimized using response surface methodology based on central composite design. Hydrophobic DES was prepared by mixing acetic acid with DL-menthol (1:1 M ratio) by sonication together with 50 mg of oleic acid-coated Fe_3O_4 nanoparticles, as magnetic nanoparticles, in 1 mL volume of DES was dispersed. For preparation of oleic acid-coated Fe_3O_4 nanoparticles, after treating $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ in ammonium hydroxide solution, Fe_3O_4 magnetic nanoparticles were coated with oleic acid by mixing 0.5 g of Fe_3O_4 nanoparticles with 10 % v/v of the acid, followed by the formation of the viscous solution via vigorous stirring at 150 rpm for 2 h. Under the optimum extraction conditions, the LOD and LOQ were 1.35 ng mL^{-1} and 4.57 ng mL^{-1}, respectively, with linearity in the range of 5–900 ng mL^{-1} and RSD% better than 4.2 %. The extraction efficiencies of mefenamic acid in urine samples were between 80.25 % and 97.44 % with an RSD<4.60 %.

In another application of using ferrofluids for microextraction, a hydrophobic MDES-ferrofluid method was prepared by Ghasemi, et al [77] and employed for dispersive LPME of cobalt from tap water, bottled, mineral water, seawater, and river water samples. After fully optimization of the extraction method, and by using a flame atomic absorption spectrometer for quantitative analysis, the limit of detection and enrichment factor were 0.7 and 50 mg/L, respectively. The relative standard deviation was 2.6 %. Ferrofluid was prepared from Fe_3O_4 modified with sodium dodecyl benzene sulfonate and menthol/decanoic acid hydrophobic DES. The obtained ferrofluid showed lower density than water and high hydrophobicity and stability during the extraction. For synthesis of hydrophobic ferrofluid, co-precipitation were prepared by Fe_3O_4 nanoparticle following reaction of $FeCl_3$ and $FeCl_2$ in ammonia solution. Then, 0.5 g of 1.0 % solution of sodium dodecyl benzene

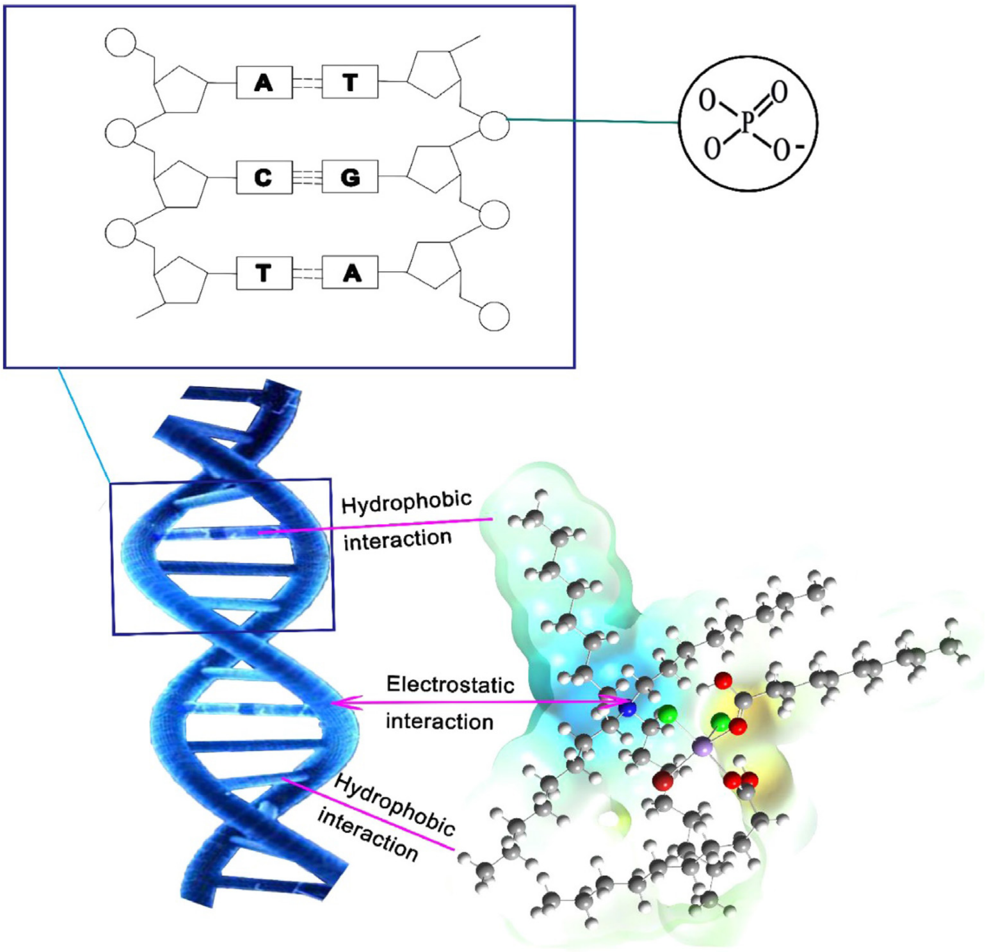


Fig. 7. Interactions between DNA and the hydrophobic MDES (from ref [4], with permission).

sulfonate was added to a beaker containing 3.0 g of Fe_3O_4 nanoparticles, followed by 15-min sonication. The magnetic solid was collected using a magnetic bar and dispersed in hydrophobic DES carrier and treated by ultrasonication. Hydrophobic DES was prepared as 1:1 ratio of menthol:decanoic acid.

Although DES based ferrofluid showed good performance in the field of microextraction, its performance was limited by its poor dispersion stability. In 2021, Piao et al. proposed an in-situ formed MDES combined with the LPME method, which had both the magnetic characteristics of the ferrofluid and the good dispersion of the extraction medium [23]. This new type of magnetic DES showed a high affinity and could greatly simplify the extraction process through magnetic separation technology. Five triazine herbicides, desmetryn, secbumeton, terbumeton, terbuthylazine and prometryn were determined in rice and maize after their dispersive liquid–liquid extraction using a TBAB:ethylene glycol:$FeCl_4$ MDES before HPLC analysis. DES were prepared by mixing ethylene glycol and tetrabutylammonium chloride at four different molar ratio (1:1, 2:1, 3:1 and 4:1) and heated for 30 min at 80 °C. 250 µL of this DES (molar ratio of ethylene glycol to tetrabutylammonium chloride 2:1) were added to 4 mL *n*-hexane extract of the sample solution and vortexed. After adsorption, 40 mg of iron chloride were added in order to in-situ formation of MDES, following by addition of 90 mg of carbonyl iron powder to enhance the magnetic properties. Finally, by using an external magnet, phase separation was performed. Parameters affecting extraction were fully studied and optimized and under optimal conditions, calibration curves for the target triazine herbicides were obtained in the ranges of 5–1000 ng g^{-1}, with correlation coefficients greater than 0.991. The limits of detection and quantification were in the range of 1.49–3.10 ng g^{-1} and 4.96–10.34 n g g^{-1}, respectively. The precision of intra-day and inter-day were under 6.2 % and 9.6 %, respectively, and the precision between laboratories were lower than 7.5 %. The accuracy of the method varied from 84.9 to 117.5 %.

The same methodology was used by Rastbood, et al. in 2020 [78] for drug meloxicam which was determined in human blood plasma and urine samples by HPLC analysis with a ferrofluid magnetic dispersive micro-solid phase extraction method based on a DES as a carrier. Extracting ferrofluid was prepared by mixing silica-coated magnetic nanoparticles with ethylene glycol/ChCl DES as carrier. To prepare this extracting ferrofluid, Fe_3O_4 magnetic nanoparticles were prepared with a procedure similar to that used in ref [76]. Functionalized silica magnetic nanoparticles were prepared and mixed with a DES which was prepared by mixing ChCl as the HBA and ethylene glycol as the HBD at different molar ratios. The mixture was placed in a water bath at 80 °C for 10 min. During this step, the chlorine atom of ChCl formed a hydrogen bond with the hydrogen atom of ethylene glycol. Thus, the DES was gradually formed in the entire solution. To perform MDES micro-solid phase extraction, 2 mg of the $SiO_2@Fe_3O_4$ nanoparticles were dispersed in 250 mL of DES (ChCl:ethylene glycol) followed by sonication until a uniform ferrofluid was achieved. Then, the ferrofluid was quickly injected into 10 mL of the sample solution using a glass syringe to form a dark suspension. After the adsorption process, the adsorbent was separated from the solution using a magnet and target analyte eluted with ethanol, from that, 20 µL of was injected into a HPLC. 250-fold excess of sodium, potassium, and calcium and 1000-fold excess of urea, thiourea, glucose, and sucrose had no significant effect on the extraction of mefenamic determination thus evidencing the selectivity. Analytical features of the method were as: linear ranges of 10–500 µg/L with extraction recoveries above 89.2 %, limit of detections was < 3.0 µg/L, 44.6 folds enrichment factors and RSDs lower than 6.2 %.

Magnetic dispersive micro-solid-phase extraction based on MDES applied for the extraction of morin in apple and grape juices, diluted and acidic extract of dried onion and green tea infusion samples [79], warfarin in biological samples [80] and phenolic compounds in fruit juice [80]. While the carrier used in the extracting ferrofluid were different, the same protocol of preparation of the MDES was followed in all cases.

It was reported HPLC determination of oxycycline in urine, blood plasma and milk by a ferrofluid prepared by adding Fe_3O_4 magnetic nanoparticles to a hydrophobic DES prepared by mixing octanoic acid and DL-menthol at 1:1 M ratio [81].

For detection of drugs by HPLC in biological fluids, magnetic nanoparticles (mainly Fe_3O_4) were treated with different DESs that featured various polarities and used for liquid phase microextraction in different modes. Extraction and separation can be performed rapidly without need of centrifugation. However, no information is provided if during the desorption step of analytes, MDES are also washed out and enter into the chromatographic columns.

Ultrasonic assisted microextraction is the method of choice when it comes to the extraction of different analytes with MDES from foodstuff. Enrichment factors up to 50 with extraction time of<3 min achieved by using these methods.

ChCl:p-cresol:$FeCl_3$ MDES was employed for ultrasound assisted liquid–liquid microextraction of hexanal and heptanal from edible oil samples followed by gas chromatography [20]. The analytical protocol was as follows: 1.5 mL of oil sample diluted with *n*-hexane for reduction of its viscosity were mixed with 40 µL of MDES by sonication. After extraction, MDES droplets were collected by placing a magnetic rod (B = 0.66 T). Analytes were back extracted to cyclohexane:ethyl acetate; 1:1 v/v and 1 µL of the back-extraction solvent was injected into the GC–FID system for analysis.

In a very recently published paper [82], for the first time, a ternary MDES was used as the extraction solvent for enantioselective determination of chiral mefentrifluconazole fungicide in cereal samples. In this report, Jia and colleagues applied a dispersive liquid–liquid microextraction method in order to selectively extract mefentrifluconazole before its determination by HPLC. The ternary MDES [octyltrimethylammonium bromide][cobalt chloride][acetic acid] was synthesized at a molar ratio of 1: 0.06: 5 as the extractant. In fact, acetic acid was functioned as the dispersant to promote the in situ dispersion of binary MDES of octyltrimethylammonium bromide and cobalt chloride. One important feature of this method is its fastness. The dispersion and separation procedures were completed only in 30 s, because MDES is generated in situ inside the sample solution. Characteristics of the analytical properties of this method evinced that the linearity of the analyte was within the range of 0.01–2 µg g^{-1} with R^2 values greater than 0.999. The LOD and LOQ of mefentrifluconazole enantiomers were 0.003 µg g^{-1} and 0.01 µg g^{-1}. The RSDs were 1.5–1.8 % for intra-day analysis and 2.9–3.1 % for inter-day analysis. Extraction recovery values obtained for S-mefentrifluconazole and R-mefentrifluconazole were 82.9–95.0 %. no information provided regarding the possibility of reusability of the method or the extraction enrichment factor.

Table 2 summarizes the main aspects of the articles published on analytical microextraction application of MDESs. As can be seen, there are unique advantages for microextraction using MDESs, such as replacing the centrifugation step with a magnet for separation, simple synthetic processes of MDES and lower price of them. Moreover, components used for preparation of MDESs mainly consist of environmentally friendly materials, in most of the cases, choline chloride. However, in many instances, still there is a need for shaking, vortexing, microwaving, and ultrasonication for extraction which prolongs the pretreatment time and is inconvenient. Moreover, reusability of the extractant is generally limited to 3 times. Low recovery is another drawback of using

MDESs as microextraction media. Almost all of the methods reported recoveries lower than 95 %, even as low as 61 %. Still with this low recovery, excellent enrichment factors, up to 550 folds were achieved.

4.2. Catalyst preparation

Tamaddon and Tadayonfar [83] prepared and characterized a magnetic gemini-surfactant-based deep eutectic from a synthetic gemini-surfactant and $FeCl_3{\cdot}6H_2O$ as HBA and HBD components. They replaced a magnetically-separable surfactant prepared by incorporation of the magnetic complex anion of $[FeCl_4]^-$ in surfactant-based DES to be used in benzoin condensation and multi-component synthesis of pyrrole derivatives. In their protocol, water was added at the end of the reaction and the magnetic aqueous solution of DES was isolated by an external magnet, and the precipitated catalyst was filtered and washed with water. They prepared this catalyst to address reusability issues and recovery drawbacks of acid catalysts in aqueous media. Efficacy could be improved by hosting of surface-active gemini-surfactants in the structure of the catalyst instead of simple surfactants due to their lower critical micelle concentration, higher polarity, and their self-assembly. The cost of production of the catalyst was also lower and recovery of this viscose liquefy catalyst is simply by using an external magnet. The catalyst could be reused without loss of its activity even after four consequent cycles. In another report [84], Tamaddon and Khorram used magnetic-responsive deep eutectic catalyst based on Co^{2+}/ChCl for the synthesis of tetrahydropyrazolopyridines and pyrroles in water. They examined the components at different mole ratios in the solid–liquid equilibrated mixtures of $CoCl_2{\cdot}6H_2O$ and ChCl followed by vacuum evaporation. Among these complexes, the bluish complex $2ChCl{\cdot}2Ch^+{:}CoCl_4^{2-}$ (Co_4ChDES), given at 1:4 mol ratio of $CoCl_2$:ChCl showed a very deep decrease in melting point and paramagnetic properties. After full characterization, they found that the structure of this MDES is so that the anionic complex $CoCl_4^{2-}$ provides magnetically recovering of Co_4ChDES in cooperation with the four choline groups, which are HBA and HBD components of this MDES. A vibrating sample magnetometery curve showed that the prepared MDES had paramagnetic properties with a magnetic saturation of 224 memu/g. This prepared MDES represented high catalytic performance in the water-based multi-component reactions for the synthesis of substituted tetrahydropyrazolopyridines and pyrroles under mild conditions. The authors showed that besides high efficiency, simple recovery, and reusability of this catalyst, it is also non-corrosive. This value is higher than gemini surfactant cobalt complex they reported previously [21]. Due to the blue color of MDES and high magnetic saturation, the authors claimed that there is a tetrahedral magnetic anionic complex $CoCl_4^{2-}$in the structure of DES formed at $CoCl_2{\cdot}4ChCl$ and hence proposed the structure indicated in Fig. 8 for their prepared MDES.

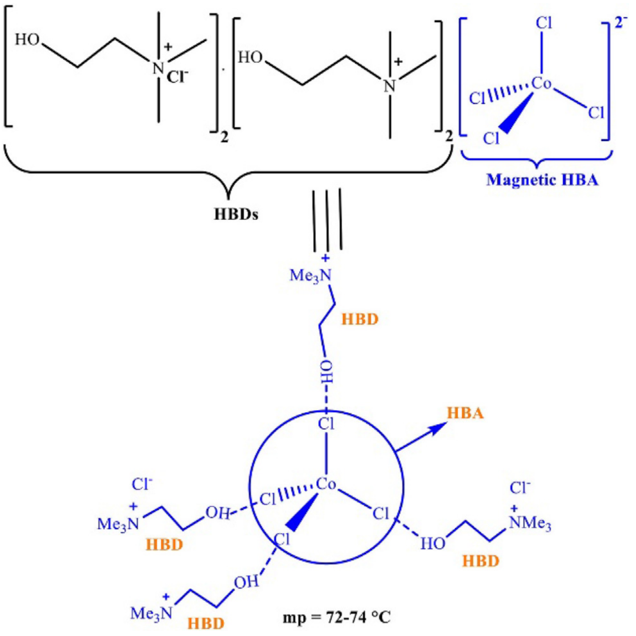


Fig. 8. The proposed formula for $CoCl_4^{2-}$.2Ch$^+$·2ChCl (from ref [71], with permission).

The reported studies clearly show that DES can be used as an appropriate media to improve catalyst reactions and that the incorporation of metal chloride to DES structure offers a possibility for the recovery of catalysts after their use in a cheap and fast way.

5. Conclusion and outlook

In recent years, the number of papers and studies on “green” solvents, i.e. deep eutectic solvents, has increased significantly. Nevertheless, there are still a very limited number of DES with magnetic properties. Magnetic susceptibility is a very useful property in many laboratory and industrial application in order to improve extraction, microextraction, or catalyst use due to the fact that allows easier phase separation through a magnetic field without a tedious centrifugation step. Therefore, an increase in research into new MDES combinations can be expected in a near future. Since MDES are still not commercially available, and information about the physicochemical properties of the already known MDES complexes is very limited, a lot of effort still needs to be done to gain a better insight into the MDES structures and their impact on properties. There is a lack of detailed information on polarity, surface tension, conductivity, thermal stability, magnetic susceptibility, viscosity, and density of MDES, as well as the influence of temperature or water addition on these parameters. So, the knowledge about these parameters is necessary to favor their subsequent applications. Based on the physicochemical parameters of MDES examined so far, we can assume that they may in the future replace many of the currently used toxic organic solvents. However, in order to consider MDES as a “green” alternative to conventional solvents, it is essential to perform MDES toxicity, biotoxicity, and volatility studies, which clearly evidence these aspects.

Current applications of MDES presented in the literature are limited to processes such as microextraction, extraction, or catalysts synthesis. However, taking into account the use of other magnetic solvents, such as magnetic ionic liquids, we can expect a significant increase of applications in the future, including in the polymer industry for the production of nanostructures and reduced dimensionality materials, or in the electronic industry as new electrochromic materials for the manufacturing of different electronic devices (information displays, anti-glare rearview of automobiles, and smart windows), as well as increasing the range of applications of MDES in separation processes. In this aspect, the future is open and research in this field must advance both, fundamental characterization and their application.

CRediT authorship contribution statement

Patrycja Makoś-Chełstowska: Conceptualization, Writing – original draft, Writing – review & editing, Visualization, Supervision. **Massoud Kaykhaii:** Writing – original draft, Writing – review & editing. **Justyna Płotka-Wasylka:** Writing – review & editing. **Miguel de la Guardia:** Writing – review & editing.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Financial support of these studies from Gdańsk University of Technology by the DEC-12/2021/IDUB/II.AMERICIUM grant under the Americium International Career Development - 'Excellence Initiative - Research University' program is gratefully acknowledged.

Prof. Massoud Kaykhaii acknowledges the Polish National Agency for Academic Exchange (NAWA) under the Ulam Programme (Agreement No. PPN/ULM/2020/1/00014/DEC/1) for their financial support.

References

[1] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, Chem. Commun. (2003) 70–71, https://doi.org/10.1039/b210714g.

[2] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep eutectic solvents (DESs) and their applications, Chem. Rev. 114 (2014) 11060–11082, https://doi.org/10.1021/cr300162p.

[3] Y. Wang, Y. Hou, W. Wu, D. Liu, Y. Ji, S. Ren, Roles of a hydrogen bond donor and a hydrogen bond acceptor in the extraction of toluene from: N -heptane using deep eutectic solvents, Green Chem. 18 (2016) 3089–3097, https://doi.org/10.1039/c5gc02909k.

[4] X. Wang, M. Liu, F. Peng, X. Ding, Hydrophobic magnetic deep eutectic solvent: synthesis, properties, and application in DNA separation, J. Chromatogr. A 1659 (2021), https://doi.org/10.1016/J.CHROMA.2021.462626 462626.

[5] M.Á. Aguirre, A. Canals, Magnetic deep eutectic solvents in microextraction techniques, TrAC Trends Anal. Chem. 146 (2022), https://doi.org/10.1016/J.TRAC.2021.116500 116500.

[6] K.D. Clark, O. Nacham, J.A. Purslow, S.A. Pierson, J.L. Anderson, Magnetic ionic liquids in analytical chemistry: a review, Anal. Chim. Acta. 934 (2016) 9–21, https://doi.org/10.1016/J.ACA.2016.06.011.

[7] M. Sajid, Magnetic ionic liquids in analytical sample preparation: a literature review, TrAC Trends Anal. Chem. 113 (2019) 210–223, https://doi.org/10.1016/J.TRAC.2019.02.007.

[8] E. Santos, J. Albo, A. Rosatella, C.A.M. Afonso, Á. Irabien, Synthesis and characterization of Magnetic Ionic Liquids (MILs) for CO2 separation, J. Chem. Technol. Biotechnol. 89 (2014) 866–871, https://doi.org/10.1002/jctb.4323.

[9] A. Joseph, G. Zyła, V.I. Thomas, P.R. Nair, A.S. Padmanabhan, S. Mathew, Paramagnetic ionic liquids for advanced applications: a review, J. Mol. Liq. 218 (2016) 319–331, https://doi.org/10.1016/J.MOLLIQ.2016.02.086.

[10] T. Khezeli, A. Daneshfar, Synthesis and application of magnetic deep eutectic solvents: novel solvents for ultrasound assisted liquid-liquid microextraction of thiophene, Ultrason. Sonochem. 38 (2017) 590–597, https://doi.org/10.1016/J.ULTSONCH.2016.08.023.

[11] D. Yue, Y. Jing, J. Sun, X. Wang, Y. Jia, Structure and ion transport behavior analysis of ionic liquid analogues based on magnesium chloride, J. Mol. Liq. 158 (2011) 124–130, https://doi.org/10.1016/J.MOLLIQ.2010.11.005.

[12] H. Wang, Y. Jing, X. Wang, Y. Yao, Y. Jia, Ionic liquid analogous formed from magnesium chloride hexahydrate and its physico-chemical properties, J. Mol. Liq. 163 (2011) 77–82, https://doi.org/10.1016/J.MOLLIQ.2011.08.004.

[13] Y. Liu, J.B. Friesen, J.B. McAlpine, D.C. Lankin, S.N. Chen, G.F. Pauli, Natural deep eutectic solvents: properties, applications, and perspectives, J. Nat. Prod. 81 (2018) 679–690, https://doi.org/10.1021/acs.jnatprod.7b00945.

[14] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jérôme, Deep eutectic solvents: Syntheses, properties and applications, Chem. Soc. Rev. 41 (2012) 7108–7146, https://doi.org/10.1039/c2cs35178a.

[15] A. Roda, A.A. Matias, A. Paiva, A.R.C. Duarte, Polymer science and engineering using deep eutectic solvents, Polymers (Basel) 11 (2019) 1–22, https://doi.org/10.3390/polym11050912.

[16] V. Abbott, A.P., Capper, G., Davies, D.L., Rasheed, R.K. & Tambyrajah, Novel Solvent Properties of Choline Chloride /Urea Mixtures, Chem. Commun. 0 (2003) 70–71. https://doi.org/https://doi.org/10.1021/ja048266j.

[17] F. Peng, M. Liu, X. Wang, X. Ding, Synthesis of low-viscosity hydrophobic magnetic deep eutectic solvent: selective extraction of DNA, Anal. Chim. Acta 1181 (2021), https://doi.org/10.1016/J.ACA.2021.338899 338899.

[18] P. Makoś, E. Słupek, J. Gębicki, Hydrophobic deep eutectic solvents in microextraction techniques–a review, Microchem. J. 152 (2020) 104384.

[19] X. Dai, X. Qiang, J. Li, T. Yao, Z. Wang, H. Song, Design and functionalization of magnetic ionic liquids surfactants (MILSs) containing alkyltrimethylammonium fragment, J. Mol. Liq. 277 (2019) 170–174, https://doi.org/10.1016/J.MOLLIQ.2018.12.096.

[20] S. Babaee, A. Daneshfar, Magnetic deep eutectic solvent-based ultrasound-assisted liquid-liquid microextraction for determination of hexanal and heptanal in edible oils followed by gas chromatography-flame ionization detection, Anal. Methods 10 (2018) 4162–4169, https://doi.org/10.1039/c8ay01058g.

[21] C. Li, J. Zhang, Z. Li, J. Yin, Y. Cui, Y. Liu, G. Yang, Extraction desulfurization of fuels with "metal ions" based deep eutectic solvents (MDESs), Green Chem. 18 (2016) 3789–3795, https://doi.org/10.1039/c6gc00366d.

[22] Z.S. Gano, F.S. Mjalli, T. Al-Wahaibi, Y. Al-Wahaibi, I.M. AlNashef, Extractive desulfurization of liquid fuel with FeCl3-based deep eutectic solvents: experimental design and optimization by central-composite design, Chem. Eng. Process. - Process Intensif. 93 (2015) 10–20, https://doi.org/10.1016/j.cep.2015.04.001.

[23] H. Piao, Y. Jiang, Z. Qin, P. Ma, Y. Sun, X. Wang, D. Song, Q. Fei, Application of an in-situ formulated magnetic deep eutectic solvent for the determination of triazine herbicides in rice, Talanta 222 (2021), https://doi.org/10.1016/J.TALANTA.2020.121527 121527.

[24] D.E. Crawford, L.A. Wright, S.L. James, A.P. Abbott, Efficient continuous synthesis of high purity deep eutectic solvents by twin screw extrusion, Chem. Commun. 52 (2016) 4215–4218, https://doi.org/10.1039/c5cc09685e.

[25] M.C. Gutiérrez, M.L. Ferrer, C.R. Mateo, F. Del Monte, Freeze-drying of aqueous solutions of deep eutectic solvents: a suitable approach to deep eutectic suspensions of self-assembled structures, Langmuir 25 (2009) 5509–5515, https://doi.org/10.1021/la900552b.

[26] C. Florindo, F.S. Oliveira, L.P.N. Rebelo, A.M. Fernandes, I.M. Marrucho, Insights into the synthesis and properties of deep eutectic solvents based on cholinium chloride and carboxylic acids, ACS Sustain. Chem. Eng. 2 (2014) 2416–2425, https://doi.org/10.1021/sc500439w.

[27] L.J.B.M. Kollau, M. Vis, A. Van Den Bruinhorst, A.C.C. Esteves, R. Tuinier, Quantification of the liquid window of deep eutectic solvents, Chem. Commun. 54 (2018) 13351–13354, https://doi.org/10.1039/c8cc05815f.

[28] H. Vanda, Y. Dai, E.G. Wilson, R. Verpoorte, Y.H. Choi, Green solvents from ionic liquids and deep eutectic solvents to natural deep eutectic solvents, Comptes Rendus Chim. 21 (2018) 628–638, https://doi.org/10.1016/j.crci.2018.04.002.

[29] Z. Chen, T.L. Greaves, G.G. Warr, R. Atkin, Mixing cations with different alkyl chain lengths markedly depresses the melting point in deep eutectic solvents formed from alkylammonium bromide salts and urea, Chem. Commun. 53 (2017) 2375–2377, https://doi.org/10.1039/c7cc00201g.

[30] A. Mackowiak, P. Galek, K. Fic, Deep eutectic solvents for high-temperature electrochemical capacitors, ChemElectroChem. 8 (2021) 4028–4037, https://doi.org/10.1002/celc.202100711.

[31] P.J. Smith, C.B. Arroyo, F. Lopez Hernandez, J.C. Goeltz, Ternary deep eutectic solvent behavior of water and urea choline chloride mixtures, J. Phys. Chem. B. 123 (2019) 5302–5306, https://doi.org/10.1021/acs.jpcb.8b12322.

[32] N. Subba, P. Sahu, N. Das, P. Sen, Rational design, preparation and characterization of a ternary non-ionic room-temperature deep eutectic solvent derived from urea, acetamide, and sorbitol, J. Chem. Sci. 133 (2021), https://doi.org/10.1007/s12039-020-01866-2.

[33] D.J.G.P. Van Osch, L.F. Zubeir, A. Van Den Bruinhorst, M.A.A. Rocha, M.C. Kroon, Hydrophobic deep eutectic solvents as water-immiscible extractants, Green Chem. 17 (2015) 4518–4521, https://doi.org/10.1039/c5gc01451d.

[34] M. Jablonský, A. Škulcová, A. Ház, J. Šima, V. Majová, Long-term Isothermal Stability of Deep Eutectic Solvents, BioResources. 13 (2018) 7445–7559. https://doi.org/10.15376/BIORES.13.4.7545-7559.

[35] A.P.R. Santana, J.A. Mora-Vargas, T.G.S. Guimarães, C.D.B. Amaral, A. Oliveira, M.H. Gonzalez, Sustainable synthesis of natural deep eutectic solvents (NADES) by different methods, J. Mol. Liq. 293 (2019), https://doi.org/10.1016/J.MOLLIQ.2019.111452 111452.

[36] O.G. Polyachenok, E.N. Dudkina, L.D. Polyachenok, Thermal stability and thermodynamics of manganese(II) chloride monohydrate, J. Chem. Thermodyn. 41 (2009) 414–419, https://doi.org/10.1016/j.jct.2008.10.011.

[37] T. El Achkar, H. Greige-Gerges, S. Fourmentin, Basics and properties of deep eutectic solvents: a review, Environ. Chem. Lett. 19 (2021) 3397–3408, https://doi.org/10.1007/s10311-021-01225-8.

[38] H. Wang, Y. Jia, X. Wang, Y. Yao, Y. Jing, Physical-chemical properties of nickel analogs ionic liquid based on choline chloride, J. Therm. Anal. Calorim. 115 (2014) 1779–1785, https://doi.org/10.1007/s10973-013-3398-3.

[39] V.S. Protsenko, L.S. Bobrova, F.I. Danilov, Physicochemical properties of ionic liquid mixtures containing choline chloride, chromium (III) chloride and water: effects of temperature and water content, Ionics (Kiel). 23 (2017) 637–643, https://doi.org/10.1007/s11581-016-1826-7.

[40] L.S. Bobrova, F.I. Danilov, V.S. Protsenko, Effects of temperature and water content on physicochemical properties of ionic liquids containing CrCl3·xH2O and choline chloride, J. Mol. Liq. 223 (2016) 48–53, https://doi.org/10.1016/J.MOLLIQ.2016.08.027.

[41] Z.H. Pebdani, R. Hajipour, Y. Ghayeba, Thermo Physical Properties of Lewis Acidic Ionic Liquids [Bu 3 NBn] Cl-2(MClm), (MClm= AlCl 3, FeCl 3, CuCl 2, SnCl 4, ZnCl 2) binary mixtures with DMSO at Temperatures from (298.15 to 363.15) K, Int. J. Anal Med. Chem. 1 (2019) 1–12.

[42] F. Chemat, H. Anjum, A.M. Shariff, P. Kumar, T. Murugesan, Thermal and physical properties of (Choline chloride + urea + l-arginine) deep eutectic solvents, J. Mol. Liq. 218 (2016) 301–308, https://doi.org/10.1016/J.MOLLIQ.2016.02.062.

[43] A. Hayyan, F.S. Mjalli, I.M. Alnashef, T. Al-Wahaibi, Y.M. Al-Wahaibi, M.A. Hashim, Fruit sugar-based deep eutectic solvents and their physical properties, Thermochim. Acta 541 (2012) 70–75, https://doi.org/10.1016/j.tca.2012.04.030.

[44] A.P. Abbott, G. Capper, S. Gray, Design of improved deep eutectic solvents using hole theory, ChemPhysChem. 7 (2006) 803–806, https://doi.org/10.1002/cphc.200500489.

[45] H. Wang, Y. Jing, X. Wang, Y. Yao, Y. Jia, Structure and physico-chemical properties of three analogous ionic liquids containing magnesium chloride, J. Mol. Liq. 170 (2012) 20–24, https://doi.org/10.1016/J.MOLLIQ.2012.03.017.

[46] F.I. Danilov, V.S. Protsenko, A.A. Kityk, D.A. Shaiderov, E.A. Vasil'eva, U.P. Kumar, C.J. Kennady, Electrodeposition of nanocrystalline nickel coatings from a deep eutectic solvent with water addition, Prot. Met. Phys. Chem. Surf. 53 (6) (2017) 1131–1138.

[47] R. Haghbakhsh, K. Parvaneh, S. Raeissi, A. Shariati, A general viscosity model for deep eutectic solvents: The free volume theory coupled with association equations of state, Fluid Phase Equilib. 470 (2018) 193–202, https://doi.org/10.1016/j.fluid.2017.08.024.

[48] L.C. Tomé, D. Mecerreyes, Emerging ionic soft materials based on deep eutectic solvents, J. Phys. Chem. B 124 (2020) 8465–8478, https://doi.org/10.1021/acs.jpcb.0c04769.

[49] M. Hirao, H. Sugimoto, H. Ohno, Preparation of novel room-temperature molten salts by neutralization of amines, J. Electrochem. Soc. 147 (2000) 4168, https://doi.org/10.1149/1.1394036.

[50] T.L. Greaves, C.J. Drummond, Protic ionic liquids: properties and applications, Chem. Rev. 108 (2008) 206–237, https://doi.org/10.1021/cr068040u.

[51] R. Yusof, E. Abdulmalek, K. Sirat, M.B.A. Rahman, Tetrabutylammonium bromide (TBABr)-based deep eutectic solvents (DESs) and their physical properties, Molecules 19 (2014) 8011–8026, https://doi.org/10.3390/molecules19068011.

[52] A.P. Abbott, G. Capper, K.J. McKenzie, K.S. Ryder, Electrodeposition of zinc–tin alloys from deep eutectic solvents based on choline chloride, J. Electroanal. Chem. 599 (2007) 288–294, https://doi.org/10.1016/J.JELECHEM.2006.04.024.

[53] K.K. Kow, K. Sirat, Novel manganese(II)-based deep eutectic solvents: synthesis and physical properties analysis, Chinese Chem. Lett. 26 (2015) 1311–1314, https://doi.org/10.1016/j.cclet.2015.05.049.

[54] D. Reuter, C. Binder, P. Lunkenheimer, A. Loidl, Ionic conductivity of deep eutectic solvents: the role of orientational dynamics and glassy freezing, Phys. Chem. Chem. Phys. 21 (2019) 6801–6809, https://doi.org/10.1039/c9cp00742c.

[55] K. Shahbaz, F.S. Mjalli, M.A. Hashim, I.M. AlNashef, Prediction of the surface tension of deep eutectic solvents, Fluid Phase Equilib. 319 (2012) 48–54, https://doi.org/10.1016/j.fluid.2012.01.025.

[56] A.Y.M. Al-Murshedi, H.F. Alesary, R. Al-Hadrawi, Thermophysical properties in deep eutectic solvents with/without water, J. Phys. Conf. Ser. 1294 (5) (2019) 052041.

[57] R. Haghbakhsh, M. Taherzadeh, A.R.C. Duarte, S. Raeissi, A general model for the surface tensions of deep eutectic solvents, J. Mol. Liq. 307 (2020), https://doi.org/10.1016/J.MOLLIQ.2020.112972 112972.

[58] K.A. Kurnia, M.I.A. Mutalib, Z. Man, M.A. Bustam, Density and Surface Tension of Ionic Liquids [H2N–C2mim][PF6] and [H2N–C3mim][PF6], J. Chem. Eng. Data. (2012) 17025–17036.

[59] Y. Chen, W. Chen, L. Fu, Y. Yang, Y. Wang, X. Hu, F. Wang, T. Mu, Surface tension of 50 deep eutectic solvents: effect of hydrogen-bonding donors, hydrogen-bonding acceptors, other solvents, and temperature, Ind. Eng. Chem. Res. 58 (2019) 12741–12750, https://doi.org/10.1021/acs.iecr.9b00867.

[60] V. Andruch, P. Makoś-Chełstowska, J. Płotka-Wasylka, Remarks on use of the term "deep eutectic solvent" in analytical chemistry, Microchem. J. 179 (2022), https://doi.org/10.1016/J.MICROC.2022.107498 107498.

[61] F. Califano, N. James, Effects of viscosity on phase separation of liquid mixtures with a critical point of miscibility, J. Eng. Technol. Res. 5 (2013) 79–86.

[62] P. Makoś-Chełstowska, E. Słupek, A. Małachowska, Superhydrophobic sponges based on green deep eutectic solvents for spill oil removal from water, J. Hazard. Mater. 425 (2022), https://doi.org/10.1016/J.JHAZMAT.2021.127972 127972.

[63] P. Makoś, E. Słupek, A. Małachowska, Silica gel impregnated by deep eutectic solvents for adsorptive removal of BTEX from gas streams, Materials (Basel) 13 (2020) 1894, https://doi.org/10.3390/ma13081894.

[64] P. Shi, A. Engström, B. Sundman, Thermodynamic investigations on materials corrosion in some industrial and environmental processes, J. Environ. Sci. 23 (2011) S1–S7, https://doi.org/10.1016/S1001-0742(11)61067-X.

[65] J.E. Qu, X.P. Guo, H.R. Wang, J.Y. Huang, Corrosion behavior of pure aluminum in FeCl3 solution, Trans. Nonferrous Met. Soc. China 16 (2006) 1460–1466, https://doi.org/10.1016/S1003-6326(07)60038-7.

[66] M. Lambrecht, M.T. de Miguel, M.I. Lasanta, F.J. Pérez, Past research and future strategies for molten chlorides application in concentrated solar power technology, Sol. Energy Mater. Sol. Cells 237 (2022), https://doi.org/10.1016/J.SOLMAT.2021.111557 111557.

[67] Z.G. Shi, Y. Zhang, H.K. Lee, Ferrofluid-based liquid-phase microextraction, J. Chromatogr. A 1217 (2010) 7311–7315, https://doi.org/10.1016/J.CHROMA.2010.09.049.

[68] A.R. Zarei, M. Nedaei, S.A. Ghorbanian, Ferrofluid of magnetic clay and menthol based deep eutectic solvent: application in directly suspended droplet microextraction for enrichment of some emerging contaminant explosives in water and soil samples, J. Chromatogr. A 1553 (2018) 32–42, https://doi.org/10.1016/J.CHROMA.2018.04.023.

[69] Y. Liu, Y. Wang, Q. Dai, Y. Zhou, Magnetic deep eutectic solvents molecularly imprinted polymers for the selective recognition and separation of protein, Anal. Chim. Acta 936 (2016) 168–178, https://doi.org/10.1016/J.ACA.2016.07.003.

[70] D. Wang, X. Luo, Y. Huang, M. Wang, Z. Xia, Combined magnetic molecularly imprinted polymers with a ternary deep eutectic solvent to purify baicalein from the Scutellaria baicalensis Georgi by magnetic separation, Microchem. J. 157 (2020), https://doi.org/10.1016/J.MICROC.2020.105109 105109.

[71] Y. Zhang, H. Cao, Q. Huang, X. Liu, H. Zhang, Isolation of transferrin by imprinted nanoparticles with magnetic deep eutectic solvents as monomer, Anal. Bioanal. Chem. 410 (2018) 6237–6245, https://doi.org/10.1007/s00216-018-1232-2.

[72] F. Jamshidi, N. Nouri, H. Sereshti, M.H. Shojaee Aliabadi, Synthesis of magnetic poly (acrylic acid-menthol deep eutectic solvent) hydrogel: application for extraction of pesticides, J. Mol. Liq. 318 (2020), https://doi.org/10.1016/J.MOLLIQ.2020.114073 114073.

[73] A. Jouyban, M.A. Farajzadeh, M. Nemati, A.A. Alizadeh Nabil, M.R. Afshar Mogaddam, Preparation of ferrofluid from toner powder and deep eutectic solvent used in air-assisted liquid-liquid microextraction: application in analysis of sixteen polycyclic aromatic hydrocarbons in urine and saliva samples of tobacco smokers, Microchem. J. 154 (2020), https://doi.org/10.1016/J.MICROC.2020.104631 104631.

[74] A. Jouyban, M.A. Farajzadeh, M.R. Afshar Mogaddam, M. Nemati, A.A. Alizadeh Nabil, Ferrofluid-based dispersive liquid-liquid microextraction using a deep eutectic solvent as a support: applications in the analysis of polycyclic aromatic hydrocarbons in grilled meats, Anal. Methods 12 (2020) 1522–1531, https://doi.org/10.1039/d0ay00073f.

[75] A. Bazzaz Dilmaghani, F. Monajjemzadeh, M.R. Afshar Mogaddam, M.A. Farajzadeh, Sonochemical synthesis of deep eutectic solvent-coated magnetic nanoparticles and their application in magnetic dispersive micro solid phase extraction–dispersive liquid–liquid microextraction of polycyclic aromatic hydrocarbons from mascara, Microchem. J. 181 (2022), https://doi.org/10.1016/J.MICROC.2022.107665 107665.

[76] E.A. Dil, M. Ghaedi, A. Asfaram, Application of hydrophobic deep eutectic solvent as the carrier for ferrofluid: a novel strategy for pre-concentration and determination of mefenamic acid in human urine samples by high performance liquid chromatography under experimental design optimization, Talanta 202 (2019) 526–530, https://doi.org/10.1016/J.TALANTA.2019.05.027.

[77] A. Ghasemi, M.R. Jamali, Z. Es'haghi, Ultrasound assisted ferrofluid dispersive liquid phase microextraction coupled with flame atomic absorption spectroscopy for the determination of cobalt in environmental samples, Anal. Lett. 54 (2021) 378–393, https://doi.org/10.1080/00032719.2020.1765790.

[78] S. Rastbood, M.R. Hadjmohammadi, S.M. Majidi, Development of a magnetic dispersive micro-solid-phase extraction method based on a deep eutectic solvent as a carrier for the rapid determination of meloxicam in biological samples, Anal. Methods 12 (2020) 2331–2337, https://doi.org/10.1039/d0ay00095g.

[79] S.M. Majidi, M.R. Hadjmohammadi, Alcohol-based deep eutectic solvent as a carrier of SiO2@Fe3O4 for the development of magnetic dispersive micro-solid-phase extraction method: application for the preconcentration and determination of morin in apple and grape juices, diluted and acidic ex, J. Sep. Sci. 42 (2019) 2842–2850, https://doi.org/10.1002/jssc.201900234.

[80] N. Nooraee Nia, M.R. Hadjmohammadi, Nanofluid of magnetic-activated charcoal and hydrophobic deep eutectic solvent: application in dispersive magnetic solid-phase extraction for the determination and preconcentration of warfarin in biological samples by high-performance liquid chromatograph, Biomed. Chromatogr. 35 (2021) 1–10, https://doi.org/10.1002/bmc.5113.

[81] E. Alipanahpour Dil, M. Ghaedi, A. Asfaram, L. Tayebi, F. Mehrabi, A ferrofluidic hydrophobic deep eutectic solvent for the extraction of doxycycline from urine, blood plasma and milk samples prior to its determination by high-performance liquid chromatography-ultraviolet, J. Chromatogr. A 1613 (2020) 460695.

[82] X. Jing, H. Xue, X. Sang, X. Wang, L. Jia, Magnetic deep eutectic solvent-based dispersive liquid–liquid microextraction for enantioselectively determining chiral mefentrifluconazole in cereal samples via ultra-high-performance liquid chromatography, Food Chem. 391 (2022), https://doi.org/10.1016/J.FOODCHEM.2022.133220 133220.

[83] F. Tamaddon, S.E. Tadayonfar, A novel bi-functional surfactant-based paramagnetic deep-eutectic catalyst for improved benzoin condensation and multi-component synthesis of pyrrole derivatives, J. Mol. Liq. 280 (2019) 71–78, https://doi.org/10.1016/J.MOLLIQ.2019.01.095.

[84] F. Tamaddon, A. Khorram, New magnetic-responsive deep eutectic catalyst based on Co2+/choline chloride for the synthesis of tetrahydro-pyrazolopyridines and pyrroles in water, J. Mol. Liq. 304 (2020), https://doi.org/10.1016/J.MOLLIQ.2020.112722 112722.

[85] T. Long, Y. Deng, S. Gan, J. Chen, Application of choline chloride·xZnCl2 ionic liquids for preparation of biodiesel, Chinese J Chem. Eng. 18 (2010) 322–327, https://doi.org/10.1016/S1004-9541(08)60359-6.

[86] Z.S. Gano, F.S. Mjalli, T. Al-Wahaibi, Y. Al-Wahaibi, I.M. Alnashef, Solubility of thiophene and dibenzothiophene in anhydrous FeCl3- and ZnCl2-based deep eutectic solvents, Ind. Eng. Chem. Res. 53 (2014) 6815–6823, https://doi.org/10.1021/ie500466g.

[87] Y. Zhang, X. Lu, X. Feng, Y. Shi, X. Ji, Properties and applications of choline-based deep eutectic solvents, Prog. Chem. 25 (2013) 881–892, https://doi.org/10.7536/PC121044.