

# From Phase Change Materials to Green Solvents: Hydrophobic Low Viscous Fatty Acid–Based Deep Eutectic Solvents

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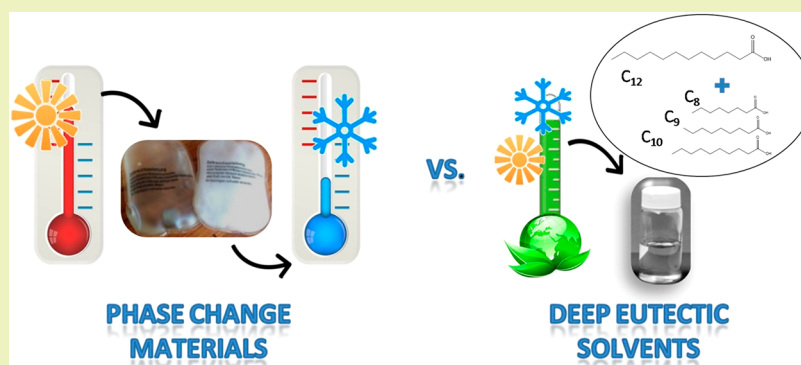
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**S** Supporting Information



**ABSTRACT:** Inspired by the use of fatty acids in development of low temperature latent heat storage materials, novel low viscous and hydrophobic deep eutectic solvents (DESs) based exclusively on fatty acids are herein proposed as sustainable solvents. Three DESs were prepared by exclusively combining fatty acids, namely octanoic acid ( $C_8$ ), nonanoic acid ( $C_9$ ), decanoic acid ( $C_{10}$ ), and dodecanoic acid ( $C_{12}$ ), which can simultaneously act as hydrogen bond donors and acceptors. The obtained fatty acid-based DESs were analyzed in order to check their structures, purities, and proportions. Water stability was also carefully evaluated through  $^1H$  NMR. Fatty-acid DESs melting point diagrams were determined by visual observation. Good agreement was obtained between the experimental eutectic point and that predicted by considering an ideal system of two individually melting compounds. Important solvent thermophysical properties, such as density and viscosity of the dried and water-saturated DESs, were measured. Finally, the removal of bisphenol A, a persistent micropollutant present in aqueous environments illustrates the potential of binary and ternary fatty acid-based DESs as extraction solvents. All prepared DESs showed good ability to extract bisphenol A from water with extraction efficiencies up to 92%.

**KEYWORDS:** Deep eutectic solvents, Fatty acids, Hydrophobicity, Water treatment, Bisphenol-A extraction

## INTRODUCTION

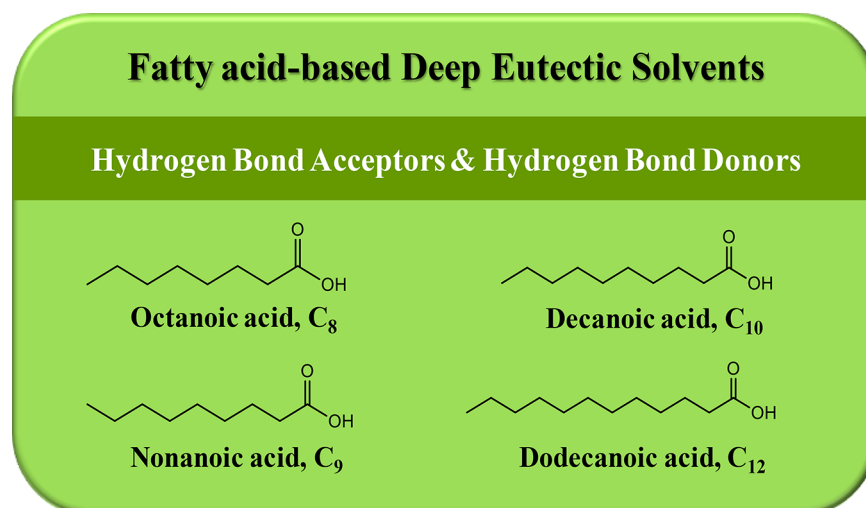
Developing a cost-effective and environmentally benign solvent is of vital importance in the chemical industry. The demand for environmentally benign, less toxic, biodegradable, natural and low-cost solvents has slowly encouraged the development of novel alternative solvents. Over the past decade, some green solvents have emerged as harmless solvents, namely supercritical fluids, biobased solvents, ionic liquids (ILs), and more recently deep eutectic solvents (DESs).<sup>1–3</sup> Eutectic mixtures are a well-known class of multicomponent solid systems, presenting melting point temperature depressions relative to their parent compounds. However, the high melting points of many eutectic mixtures hamper their application as green

solvents at room temperature. Eutectic solvents that are liquid around room temperature were scarcely reported in the literature until the beginning of the 21st century.<sup>4</sup> Only in 2003 did Abbott et al. propose eutectic mixtures as a versatile and sustainable platform of tunable solvents. In fact, these authors showed that if a salt or a solid ionic liquid is used in the mixture, a large melting point depression can be obtained, thus coining the designation deep eutectic solvents. These solvents have been emerging as a new generation of solvents with great

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**Figure 1.** Chemical structures of the compounds used for the fatty acid-based deep eutectic solvents studied in this work.

potential for a variety of applications, such as in electrochemistry and metal extraction,<sup>5</sup> nanotechnology,<sup>6</sup> stabilization of DNA,<sup>7</sup> materials chemistry,<sup>8</sup> catalysis,<sup>9</sup> and organic synthesis,<sup>10</sup> among others.

DESs have been introduced as alternatives to ionic liquids, overcoming their main disadvantages, such as high cost and toxicity, while keeping their negligible vapor pressure, easy tunability, and excellent solvation properties.<sup>11,12</sup> Although less explored, mixtures of two neutral natural compounds can also yield liquids at room temperature. Despite the fact that melting point depressions of neutral eutectic mixtures are not as deep as when ionic compounds are used, they have also adopted the unifying DES designation, since they can also be used as solvents. Choi and co-workers<sup>13</sup> have been reporting a large number of stable natural DESs, either based on charged compounds or neutral natural compounds, which are liquid at room temperature. One of the main advantages of DESs is their very simple synthetic process, which consists on mixing different proportions of two or more components, until a liquid with a melting point lower than the starting materials is obtained.<sup>14</sup> Generally, DESs are often simply prepared from binary mixtures of hydrogen bond acceptors (HBA), such as quaternary ammonium salts combined with a hydrogen bond donor (HBD), such as an amino acid,<sup>15</sup> sugar,<sup>16</sup> alcohol<sup>17</sup> or carboxylic acid.<sup>18</sup> Recently, other nonionic DESs have been reported, for example, eutectic mixtures composed of dimethylurea combined with citric acid, mannose, or L-tartaric acid.<sup>19,20</sup>

This field has greatly evolved in the last couple of years, showing a great diversity of starting compounds that form liquids at room temperature when combined in certain molar ratios,<sup>21</sup> thus providing a powerful tool to control the properties of DESs. Recently, the lack of chemical stability of hydrophilic DESs based on hydrophilic ammonium salts when in contact with water motivated the development of hydrophobic DESs as green substitutes for conventional organic solvents.<sup>22,23</sup> Diverse starting compounds have been used in hydrophobic DES preparation, ranging from long chain quaternary ammonium halides<sup>23</sup> to hydrophobic natural compounds, such as menthol<sup>24</sup> and long alkyl chain fatty acids.<sup>22,23</sup>

In this work, new natural hydrophobic DESs, composed exclusively of fatty acids, are developed. Long hydrocarbon

chain fatty acid eutectics have been largely explored as phase change materials (PCMs), for low temperature latent heat storage.<sup>25</sup> Their importance is essentially related to their good chemical stability, smaller volume change during phase transition and high latent heat of fusion and melting temperature in the desired operating range.<sup>26</sup> The phase change temperatures of fatty acid eutectics can be easily adjusted by mixing fatty acids with diverse alkyl chain lengths in suitable proportions while keeping nonreactivity, recyclability, noncorrosiveness, low cost, and the nontoxicity advantages of fatty acids.<sup>27</sup> To the best of our knowledge, no study addressed yet the preparation and use of green solvents using fatty acid PCMs starting materials. In this perspective, the goal of the present contribution is to use the same class of materials that can be modulated for heat storage applications to develop novel sustainable hydrophobic DESs to be used in water purification technologies. For that purpose, dodecanoic acid (C<sub>12</sub> acid) was combined with octanoic acid (C<sub>8</sub> acid), nonanoic acid (C<sub>9</sub> acid), and decanoic acid (C<sub>10</sub> acid) to prepare new hydrophobic sustainable solvents. The use of acids with hydrocarbon chains smaller than C<sub>8</sub> was discarded since it leads to chemically unstable DES when in contact with water, due to the leaching of the hydrophilic acids to the aqueous phase.<sup>23,25</sup> Bisphenol A (BPA), a synthetic organic chemical used as a efficient plasticizer in the processing of a number of plastics,<sup>28</sup> was chosen to illustrate the use of the prepared DES in water treatment. Despite its small concentrations in water streams, BPA has been recognized as a persistent micropollutant due to its important effect as an endocrine disruptor, leading to altered immune functions, imbalanced hormone ratios, reproductive disorders, diabetes, cardiovascular disease, and many alterations in children.<sup>29,30</sup> Binary and ternary fatty acid-based DESs were evaluated as possible extractors of BPA from water media.

## ■ EXPERIMENTAL SECTION

**Materials.** All fatty acids, namely octanoic acid (C<sub>8</sub>) (purity ≥98%), nonanoic acid (C<sub>9</sub>) (purity ≥98%), decanoic acid (C<sub>10</sub>) (purity ≥98%), and dodecanoic acid (C<sub>12</sub>) (purity ≥98%), were purchased from Sigma-Aldrich. All materials were used without further purification. In Figure 1, the chemical structures and respective acronyms of the eutectic solvents used in this work are presented. The water used was ultrapure, double distilled, passed through a reverse osmosis system, and further treated with a Milli-Q plus water purification apparatus.

**Apparatuses and Procedures. Preparation Methodology.** Mixtures of several carboxylic acids with long alkyl chains were prepared by adding different fatty acids, which can simultaneously act as hydrogen bond donors and acceptors, in a sealed glass vial at 40 °C until a homogeneous clear solution was formed. After the determination of the solid–liquid phase diagrams, proton and carbon nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) were used to check the structures and purities of the eutectic mixtures (presented in the Supporting Information (SI)). As it can be seen, all the peaks have been attributed DES components, and no extra peaks were found in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicating that no side reactions occurred and these DES are pure.

**Solid–Liquid Phase Diagram Determination.** Mixtures of different fatty acids (HBA and HBD) were prepared in the whole composition range, allowing the measurement of the solid–liquid phase diagrams of these new DESs. The  $(T, x)$  phase diagrams were measured in a glass flask using a visual methodology, at atmospheric pressure, under constant stirring. The eutectic systems compositions were determined by weighting, at room temperature, all components within  $\pm 10^{-4}$  g using an analytical balance model AX223 from Ohaus.

Briefly, mixtures in varying molar proportions of the HBD and HBA were prepared into several glass flasks, as previously described. Then, the prepared eutectic mixtures with different compositions were heated in an oil bath under stirring using a heating plate until the complete melting of the mixtures was observed. After this first heating cycle, the temperature was turned off and during the cooling cycle, and temperatures corresponding to the first crystal appearance were recorded. The temperature was measured with a Pt100 probe with a precision of  $\pm 0.1$  °C. For all the eutectic mixture compositions, the melting occurs over a range of temperatures in between the melting temperatures of the starting compounds. The above procedure was repeated to obtain sufficient data to construct the phase diagrams of each eutectic solvent system.

**Hydrophobicity Analysis.** In order to infer about the DESs hydrophobicity, and consequently quantify the water content in dried and saturated new eutectic solvents, mixtures containing both components (water and the eutectic mixtures) were prepared, vigorously shaken for 30 min, and left to settle for 24 h. Samples of each phase were carefully taken with a syringe, and the amount of water present in each sample was quantified. The water content present in both phases for the investigated eutectic solvents was determined by Karl Fischer titration (Metrohm 870 KF Titrino Plus), and the results are presented in Table 1.

**Table 1. Summary of Compositions and Water Content of Dried and Water-Saturated Fatty Acid-Based DESs**

			water content (wt %)	
			dried	saturated
DES (HBA + HBD)	mole ratio			
dodecanoic acid ( $\text{C}_{12}$ )	octanoic acid ( $\text{C}_8$ )	1:3	0.004	1.353
	nonanoic acid ( $\text{C}_9$ )	1:3	0.006	0.843
	decanoic acid ( $\text{C}_{10}$ )	1:2	0.019	0.523

**Liquid–Liquid Extraction of Bisphenol A.** Aqueous solutions of the micropollutant bisphenol A with a concentration of 0.05 g/dm<sup>3</sup> of concentration was prepared. Although micropollutants are present in real water samples in low concentrations, ranging from nanograms per liter to several micrograms per liter, the higher concentration of bisphenol A in the starting aqueous solution used in this work, allowed the use of a simple and direct detection technique, UV–vis spectroscopic technique. On the other hand, the use of concentrated solutions of BPA guarantees that there is no saturation of BPA in the coexisting phases when envisaging the use of the proposed technology in real water samples. Afterward, 2 mL of this solution was put into contact with equal amounts of each one of the eutectic mixtures and stirred at 300 rpm, at room temperature and pressure conditions, to maximize mass transfer. The flasks were then left for phase separation

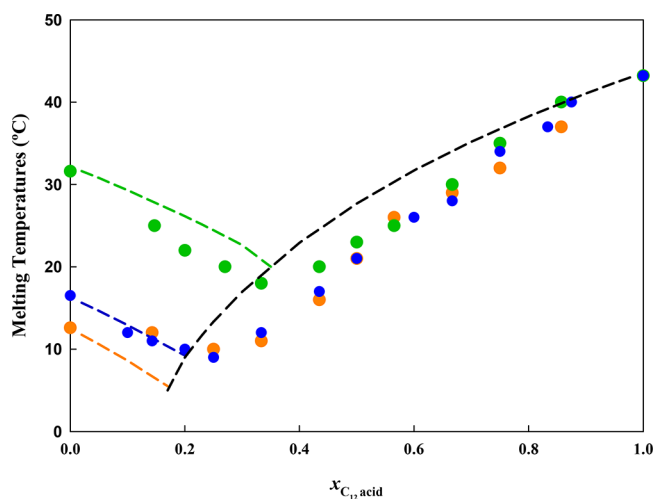
for 24 h, so that complete separation of the two phases and consequently the equilibration of pollutant between the two phases were achieved. Samples of the aqueous phase were taken and the quantification of the pollutant was carried out by UV–vis spectroscopy using a Shimadzu UV-1700, Pharma-Spec spectrophotometer, at wavelength of 276 nm for bisphenol A, by means of a calibration curve previously established. Each value of the extraction efficiency is the average of three measurements.

**Thermophysical Properties.** Measurements of viscosity and density of the DESs were carried out in the temperature range from 20 up to 80 °C and at atmospheric pressure, using an Anton Paar (model SVM 3000) automated rotational Stabinger viscometer–densimeter. The temperature uncertainty is  $\pm 0.01$  °C. The relative uncertainty of the dynamic viscosity is  $\pm 0.25\%$ , and the absolute uncertainty of the density is  $\pm 0.0005$  g·cm<sup>-3</sup>. DESs were simultaneously sampled for the water content quantification and the density and viscosity measurements.

**NMR Measurements.** All the experiments were carried out on a Bruker AVANCE 400 spectrometer operated at room temperature with 16 and 500 scans for the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra, respectively. The eutectic mixtures samples were prepared on 5 mm NMR tubes by weight approximately 30 mg of eutectic mixture and then adding 0.5 mL of deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>). The homogeneity of the sample was assured by vortex mixing.

## RESULTS AND DISCUSSION

The experimental  $(T, x)$  solid–liquid phase diagrams of mixtures of  $\text{C}_{12}$  acid with  $\text{C}_8$ ,  $\text{C}_9$ , and  $\text{C}_{10}$  acids are presented in Figure 2. It can be observed that the eutectic points of  $\text{C}_8$ : $\text{C}_{12}$



**Figure 2.** Experimental (dots) and predicted (lines) solid–liquid phase diagrams for the fatty acid-based DES studied in this work (—  $\text{C}_{12}$  acid; blue  $\text{C}_8$ : $\text{C}_{12}$ ; orange  $\text{C}_9$ : $\text{C}_{12}$ ; green  $\text{C}_{10}$ : $\text{C}_{12}$ ).

and  $\text{C}_9$ : $\text{C}_{12}$  eutectic mixtures occur approximately at 0.25 mole fraction of  $\text{C}_{12}$  acid, yielding a eutectic point at  $\text{C}_8$ : $\text{C}_{12}$  and  $\text{C}_9$ : $\text{C}_{12}$  molar proportions of (3:1), while for the  $\text{C}_{10}$ : $\text{C}_{12}$  eutectic mixture, the eutectic point happens at 0.33 mole fraction of  $\text{C}_{12}$  acid, yielding a eutectic point at  $\text{C}_{10}$ : $\text{C}_{12}$  molar proportion of (2:1). The melting temperatures of the eutectic mixtures are at 9, 9, and 18 °C for  $\text{C}_8$ : $\text{C}_{12}$ ,  $\text{C}_9$ : $\text{C}_{12}$ , and  $\text{C}_{10}$ : $\text{C}_{12}$  fatty acid DESs, respectively, validating their use as solvents at room temperature. The melting temperatures and molar mass (MM) of fatty acid–based DESs and starting materials used in this work are presented at Table 2. It can be observed that the melting point depressions of these new neutral eutectic solvents are not as large as when ionic compounds are used, 178 °C for example in the case of choline chloride and urea.<sup>31</sup> However, a

**Table 2.** Melting Temperatures and Molar Mass (MM) of Fatty Acid-Based DESs and Starting Materials Used in This Work

		MM (g/mol)	melting temperature (°C)
fatty acids	C <sub>12</sub> acid	200.32	43.2 <sup>a</sup>
	C <sub>10</sub> acid	172.26	31.6 <sup>a</sup>
	C <sub>9</sub> acid	158.23	12.6 <sup>a</sup>
	C <sub>8</sub> acid	144.21	16.7 <sup>a</sup>
fatty acid-based DESs	C <sub>8</sub> :C <sub>12</sub> (3:1)	162.91	9.00
	C <sub>9</sub> :C <sub>12</sub> (3:1)	168.75	9.00
	C <sub>10</sub> :C <sub>12</sub> (2:1)	179.28	18.0

<sup>a</sup>Values were obtained from the specifications label of each compound.

considerable lowering of the melting point, more than 10 °C, is observed when compared to the starting materials.

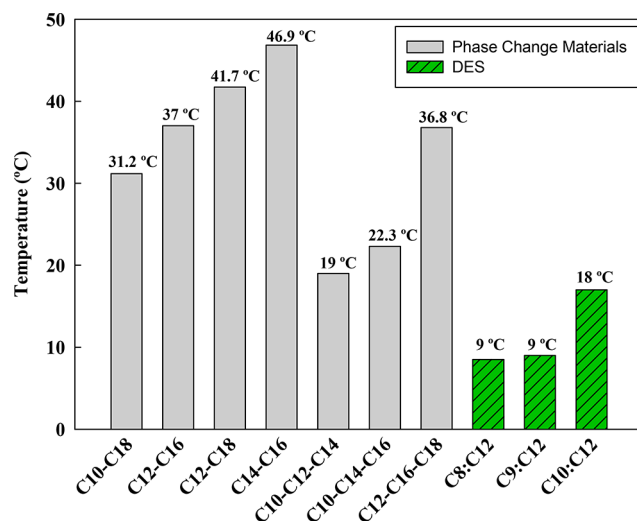
The prediction of the melting temperature of DESs is of great value, since it is often reported in the literature that a large amount of prepared DESs are solid at room temperature. A binary DES can be regarded as a binary solid–liquid equilibria system, where the two components can be independently crystallized; that is, they are not miscible in the solid state, and thus, no cocrystals are formed. A simplified phase equilibrium equation for a solid solute, designated by subscript 2 that partly dissolves in a liquid solvent, at a temperature  $T$  and a pressure  $P$  can be written as

$$x_2^l \gamma_2^l = \exp \left[ \left( \frac{\Delta H_2^{\text{sl}}}{RT_{\text{m}2}} \right) \left( \frac{T - T_{\text{m}2}}{T} \right) \right] \quad (1)$$

where  $x_2^l$  is the mole fraction of component 2 in the liquid phase (solubility),  $\gamma_2^l$  is the activity coefficient of component 2 in the liquid phase,  $T_{\text{m}2}$  and  $\Delta H_2^{\text{sl}}$  are the melting temperature (K) and melting enthalpy (J/mol) of pure component 2,  $T$  is the melting temperature (K) of the mixture, and  $R$  is the ideal gas constant (8.314 J/mol·K).

This equation takes into account that the difference between the heat capacities in the liquid and the solid state is small compared to the difference in enthalpies. Considering that the DESs here under study can be treated as ideal mixtures, the activity coefficient is set equal to unit. The use of eq 1 to predict the melting temperatures of the here studied DESs can be evaluated in Figure 2. It can be observed that eq 1 was capable of predicting both the temperature and the composition of the eutectic solvents for the three studied fatty acid mixtures. Differences in temperature of 4, 30, and 9 in percentage and in composition of 5, 7, and 2 in percentage for the C<sub>8</sub>:C<sub>12</sub>, C<sub>9</sub>:C<sub>12</sub>, and C<sub>10</sub>:C<sub>12</sub> were obtained. However, for mixtures with a composition of C<sub>12</sub> higher than that of the eutectic mixture, a poor description of the melting temperatures was obtained and thus for the full description of the entire phase diagram, an activity coefficient model needs to be used. Other authors have successfully used equations of state to describe the highly nonideal behavior of ( $T, x$ ) solid–liquid phase diagrams of DESs containing ammonium salts and fatty acids.<sup>32</sup>

In Figure 3, the melting temperatures of the three binary DESs prepared in this work are compared with those of other eutectic mixtures based on fatty acids with alkyl chains varying from C<sub>10</sub> to C<sub>18</sub>, used to develop PCMs, have melting temperatures between 15 and 45 °C.<sup>33</sup> It can be clearly observed that the melting temperatures of fatty acids eutectic



**Figure 3.** Comparison of melting temperatures of DESs studied in this work with literature values for other fatty acids used as phase change materials. The literature values are from refs 41 and 15.

mixtures can be tuned by the careful choice of the length of the fatty acids alkyl chains and their relative proportion in the mixture. The use of fatty acids with chains longer than C<sub>12</sub> leads to eutectic mixtures with high melting temperatures, which are here not classified as DESs, since they are not liquid at room temperature. Despite the small difference in the chain length between the two fatty acids used to prepare the eutectic mixtures, the differences in the pK<sub>a</sub>s of the two acids enables fatty acid with the longest alkyl chain to act as HBD, while that with the smallest chain acts as HBA.<sup>33,34</sup>

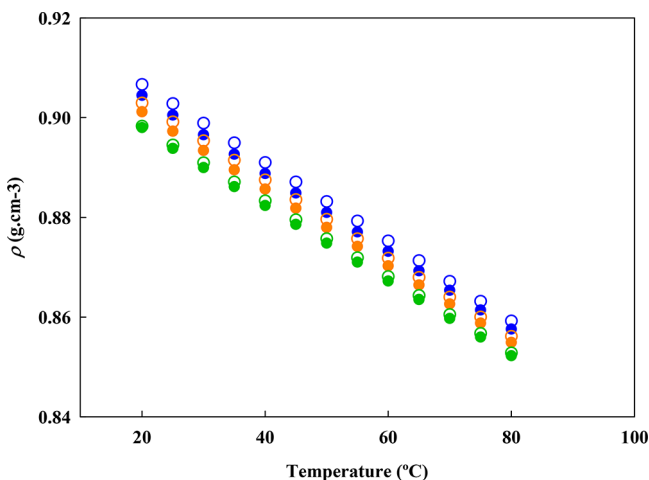
The hydrophobic character of the studied DESs was confirmed by the very low water contents of their dried and water saturated forms presented in Table 1. As expected, the longer the fatty acids chains are the higher hydrophobicity of resulting DESs. For example, for the C<sub>8</sub>:C<sub>12</sub> water contents of 0.004 and 1.353 wt % were measured for the dried and the saturated forms, while for C<sub>10</sub>:C<sub>12</sub>, water contents of 0.019 and 0.523 wt % were obtained. These new fatty acid–based DESs are the most hydrophobic reported so far in the open literature, since they present the lowest water solubility. For example, Kroon's group<sup>35</sup> published the water content of dried (0.02–0.07 wt %) and water-saturated (7–20 wt %) hydrophobic DESs composed of lidocaine and decanoic acid. In another publication,<sup>22</sup> hydrophobic DESs composed of quaternary ammonium salts and decanoic acid, values of 0.4–0.8 wt % for dried samples and 2–7 wt % for water saturated samples were reported. Ribeiro et al.<sup>24</sup> presented hydrophobic DESs based on DL-menthol and several carboxylic acids, with water contents of 0.1–1 wt % and 1.2–1.6 wt % for dried and saturated samples, respectively. More recently, Atkin's group<sup>36</sup> presented new long chain ammonium salts and urea based DESs with water contents around 0.6 wt %. In conclusion, the hydrophobicities of the new fatty acid-based DESs here reported are much higher than those published before.

NMR spectra before and after mixing DESs with water were also registered (see the SI, Figure S4–12). NMR analysis of dried and water saturated DESs showed no chemical reaction or dissociation of the fatty acids constituents and confirmed their chemical stability in the presence of water. In particular, the relative proportions of each one of the constituents is kept in the three prepared DESs, even after contacting with water.

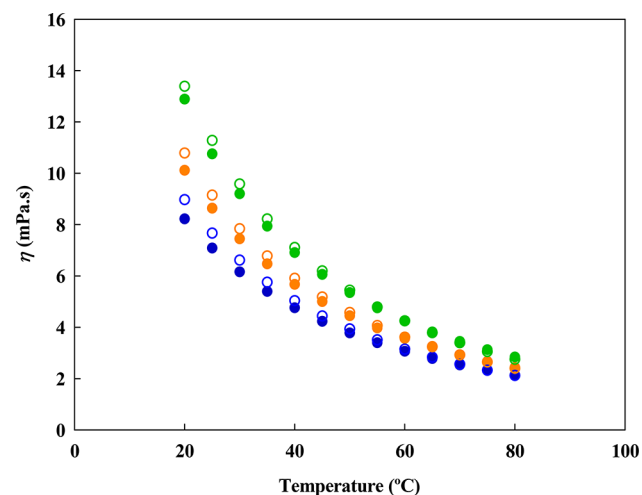


This fact means that none of the DESs components leaches to the water phase (SI, Figure S10–12).

Thermophysical properties, such as density and viscosity, are also important properties of any solvent since they influence the mass transport phenomena, thereby affecting their suitability for particular applications. The density and viscosity data of these new fatty acid-based DESs, dried and water-saturated, were obtained within the range of 20–80 °C at ambient pressure and can be found in the SI and are depicted in Figures 4 and 5, respectively. For all the samples, either in the



**Figure 4.** Experimental densities of the studied dried (filled) and water saturated (empty) fatty acid-based DESs (blue C<sub>8</sub> acid:C<sub>12</sub> acid; orange C<sub>9</sub> acid:C<sub>12</sub> acid; green C<sub>10</sub> acid:C<sub>12</sub> acid) as function of temperature.



**Figure 5.** Experimental viscosities of the new dried (filled) and water saturated (empty) fatty acid-based DESs (blue C<sub>8</sub> acid:C<sub>12</sub> acid; orange C<sub>9</sub> acid:C<sub>12</sub> acid; green C<sub>10</sub> acid:C<sub>12</sub> acid) as function of temperature.

dried or water saturated form, the density decreases linearly with temperature in the whole temperature range studied and thus eq 2 was used to describe the density temperature dependence:

$$\rho = a + bT \quad (2)$$

where  $\rho$  corresponds to density in grams per cubic centimeter,  $T$  is the temperature in K, and  $a$  and  $b$  are the fitting

parameters. The experimental density results for the dried and saturated eutectic mixtures as a function of temperature are presented in Table S2. The adjustable parameters ( $a$  and  $b$ ) were determined from the fitting of the experimental density data to eq 2 and are presented in Table S3. From Figure 4, it can be observed that the densities at 25 °C are within the range of 894–901 kg/m<sup>3</sup>. These values are lower than the densities found for most hydrophilic DESs (around 1150 kg/m<sup>3</sup>)<sup>37,38</sup> and also for the reported hydrophobic DESs (889–942 kg/m<sup>3</sup>)<sup>22</sup> and can be explained by the low densities of the starting fatty acids. As expected, the presence of water increases the density of the fatty acids DESs. However, due to the high hydrophobicity of these new DESs, their water content is very small, and thus only a very small effect of water was observed in the DESs density. The same trend was observed for the density of dried and water saturated DESs: C<sub>8</sub>:C<sub>12</sub> DES < C<sub>9</sub>:C<sub>12</sub> DES < C<sub>10</sub>:C<sub>12</sub> DES. This trend shows that as the alkyl chain of acid increases, the density of the DESs decreases in a linear manner.

The experimental viscosity values were fitted as a function of temperature, using the Vogel–Fulcher–Tammann (VFT) model:

$$\ln \eta = A_{\eta} + \frac{B_{\eta}}{(T - C_{\eta})} \quad (3)$$

where  $\eta$  is the viscosity in mPa·s,  $T$  is the temperature in °C, and  $A_{\eta}$ ,  $B_{\eta}$  and  $C_{\eta}$  are adjustable parameters. The experimental viscosity results for the dried and saturated DESs as a function of temperature are presented in Table S4 and plotted in Figure 5. The adjustable parameters of VFT model were determined from the fitting of the experimental values with temperature and are listed in Table S5. The obtained viscosities are quite low, between 7 and 11 mPa·s at 25 °C, for a very low water content, compared to other hydrophobic low viscous DESs reported in the literature, such as those based on DL-menthol and others containing several quaternary ammonium salts, which typically vary from 11 to 50<sup>24</sup> and 173 to 783 mPa·s,<sup>22</sup> respectively.

As expected, an exponential decrease of viscosity with increasing temperature was observed for all samples of DESs. Again due to the high hydrophobic character of these DESs, the viscosity values of the dried and water saturated fatty acid-based DESs are very similar. Moreover, the viscosity is strongly affected by the HBD alkyl chain of fatty acids since the shorter the alkyl chains of the fatty acid, the lower the DES viscosity, according to the following order C<sub>8</sub>:C<sub>12</sub> DES < C<sub>9</sub>:C<sub>12</sub> DES < C<sub>10</sub>:C<sub>12</sub> DES.

The activation energy was calculated based on the viscosity dependence with temperature as follows:

$$E_a = R \left( \frac{B_{\eta}}{\left( \frac{C_{\eta}^2}{T^2} - \frac{2C_{\eta}}{T} + 1 \right)} \right) \quad (4)$$

where  $\eta$  is the viscosity,  $T$  is the temperature,  $B_{\eta}$  and  $C_{\eta}$  are the adjustable parameters obtained from eq 4, and  $R$  is the universal gas constant. The values of the activation energies for the prepared eutectic solvents are presented in Table S6.

The use of eq 4 allows the discussion of the energy barrier of a fluid to shear stress,  $E_a$ , values. The higher the  $E_a$  value, the more difficult it is for the molecules/aggregates to move past each other. This can be a direct consequence of the size or

entanglement of the molecules/aggregates and/or the presence of stronger interactions within the fluid. The same trend observed in viscosity values was also observed for the  $E_a$  of dried and water saturated DESs:  $C_8:C_{12}$  DES <  $C_9:C_{12}$  DES <  $C_{10}:C_{12}$  DES. This trend shows that as the alkyl chain of acid increases, the  $E_a$  of the DES increases in a linear manner. All fatty acid-based DESs containing linear non substituted carboxylic acids have low  $E_a$  values (22 to 25 kJ/mol), in agreement with low viscosity. The  $E_a$  values obtained for water saturated DESs are similar to each other, indicating that the presence of water, even in different amounts, and in mixtures with different molar ratios, leads an easier and similar flux of the different molecules/aggregates.

Taking into account the results obtained for the prepared fatty acid-based DESs, their performance in the extraction of a persistent micropollutant, BPA, from water was studied. The one step-extraction efficiencies, EE, were calculated using eq 5, from the BPA concentration in the water phase before,  $C_{BPA,0}^{aq}$  and after the extraction,  $C_{BPA,1}^{aq}$ :

$$\%EE = \frac{C_{BPA,0}^{aq} - C_{BPA,1}^{aq}}{C_{BPA,0}^{aq}} \quad (5)$$

The one-step extraction efficiencies of BPA using the proposed binary fatty acid-based DESs are summarized in Table 3 and

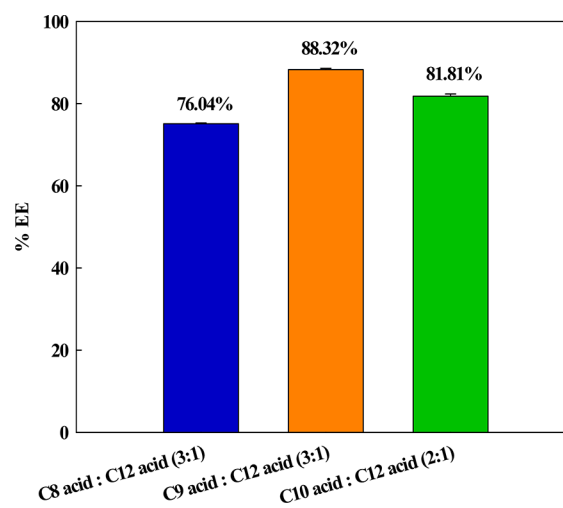
**Table 3. Extraction Efficiencies (EE %) of Bisphenol A Using Binary and Ternary Fatty Acid-Based DESs<sup>a</sup>**

fatty acid-based DESs		EE %
binary DESs	$C_8:C_{12}$ (3:1)	76.04 ± 1.13
	$C_9:C_{12}$ (3:1)	88.32 ± 0.23
	$C_{10}:C_{12}$ (2:1)	81.81 ± 0.34
ternary DESs	$C_8:C_9:C_{12}$ (1:1:1)	85.49 ± 0.86
	$C_8:C_9:C_{12}$ (1:2:1)	84.53 ± 0.43
	$C_8:C_9:C_{12}$ (2:1:1)	82.34 ± 1.10
	$C_8:C_9:C_{12}$ (3:1:1)	79.42 ± 0.54
	$C_8:C_9:C_{12}$ (3:2:1)	80.32 ± 0.78
	$C_9:C_{10}:C_{12}$ (1:1:1)	87.65 ± 1.06
	$C_9:C_{10}:C_{12}$ (1:2:1)	87.81 ± 0.67
	$C_9:C_{10}:C_{12}$ (2:1:1)	89.01 ± 0.72
	$C_9:C_{10}:C_{12}$ (2:2:1)	89.06 ± 0.34
	$C_9:C_{10}:C_{12}$ (3:1:1)	91.52 ± 0.41
	$C_9:C_{10}:C_{12}$ (3:2:1)	90.50 ± 0.57
	$C_8:C_{10}:C_{12}$ (1:1:1)	82.77 ± 1.03
	$C_8:C_{10}:C_{12}$ (2:1:1)	79.45 ± 0.46
	$C_8:C_{10}:C_{12}$ (3:1:1)	77.75 ± 0.72
	$C_8:C_{10}:C_{12}$ (3:2:1)	79.62 ± 0.58

<sup>a</sup>Stirring speed = 300 rpm, ratio DES/water = 1:1, temperature = 25 °C, mixing time = 15 min.

plotted in Figure 6. The studied hydrophobic DESs showed very high one-step extraction efficiencies (up to 92%) for BPA. Moreover, the obtained extraction efficiencies can be ordered according to the following sequence:  $C_8:C_{12}$  DES <  $C_{10}:C_{12}$  DES <  $C_9:C_{12}$  DES, showing no clear trend between the % EE and the hydrophobicity of the DESs. However, this might be linked to the fact that  $C_{10}:C_{12}$  DES has a different molar ratio (2:1) than the other two DESs (3:1).

Since DESs can be prepared from two or more components and consequently their properties can be tailored by changing the number of HBDs, ternary DESs were also prepared by addition of a second HBD to  $C_8:C_{12}$ ,  $C_9:C_{12}$ , and  $C_{10}:C_{12}$ ,



**Figure 6.** One-step extraction efficiencies (EE %) of bisphenol A using the fatty acid-based DESs developed in this work (stirring speed = 300 rpm, ratio DES/water = 1:1, temperature = 25 °C, mixing time = 15 min).

aiming at achieving higher extraction efficiencies. In this way, three families of ternary DESs were prepared by the addition of a third component (octanoic, nonanoic, and decanoic acids) to the binary DESs studied so far. The extraction of BPA from aqueous media was carried out and obtained EE % are also listed in Table 3 and presented in Figure S1 of the SI. In Figures S2–S4 a direct comparison of the EE % of BPA for each binary DESs with the corresponding ternary DESs is illustrated. Overall, the EE % obtained for the ternary DESs are between 79 and 91%, indicating that addition of a third component in the binary DESs is indeed capable to tuning the extraction efficiencies of BPA. Furthermore, the EE % obtained for the binary DESs  $C_8:C_{12}$  (76.04%) is the lowest, showing that a higher hydrophobicity is favorable in the extraction of BPA. In other words, the addition of either  $C_9$  to form  $C_8:C_9:C_{12}$  or  $C_{10}$  to form  $C_8:C_{10}:C_{12}$  enhances the EE % of BPA. This can be seen from the EE % obtained for the binary DESs  $C_8:C_{12}$  and the ternary DES  $C_8:C_9:C_{12}$  (3:1:1) and  $C_8:C_9:C_{12}$  (3:2:1), with values of 79.42% and 80.32%, respectively, with those obtained for  $C_8:C_{10}:C_{12}$  (3:1:1) and  $C_8:C_{10}:C_{12}$  (3:2:1) with values of 77.75% and 79.62%, respectively. On the other hand, it can also be observed that a decrease in the proportion of  $C_8$  in the ternary DESs leads to higher extraction efficiencies, with EE % of 79.42%, 82.34%, and 85.49% for  $C_8:C_9:C_{12}$  (3:1:1),  $C_8:C_9:C_{12}$  (2:1:1), and  $C_8:C_9:C_{12}$  (1:1:1), respectively. The same trend can be observed for the ternary DES  $C_8:C_{10}:C_{12}$  with EE % of 77.75%, 79.45%, and 82.77% for  $C_8:C_{10}:C_{12}$  (3:1:1),  $C_8:C_{10}:C_{12}$  (2:1:1), and  $C_8:C_{10}:C_{12}$  (1:1:1), respectively. Moreover, comparing the EE % of the  $C_8:C_9:C_{12}$  and  $C_8:C_{10}:C_{12}$  ternary DESs prepared in the same proportions, it can be concluded that the addition of  $C_9$  as a third component provides an higher increase of the EE % than the addition of  $C_{10}$ . However, all these extraction efficiencies are still lower than that obtained for the binary DES  $C_9:C_{12}$ , with a value of 88.32%. Nevertheless, it is still possible to further tune this EE % by the addition of  $C_{10}$ , by the maximum EE % of 91.42% obtained for  $C_9:C_{10}:C_{12}$  (3:1:1). In fact, all the ternary DES  $C_9:C_{10}:C_{12}$  yield higher efficiencies than the two other ternary DES families.

Passos et al.<sup>29</sup> also studied bisphenol-A extraction from aqueous media using in aqueous biphasic systems composed of

15 wt % of  $K_3PO_4$  + 25 wt % of imidazolium or ammonium-based ionic liquid + 60 wt % of aqueous phase, obtaining extraction efficiencies that reached 100% of extraction, in most systems, in one single step. Nevertheless, the cross contamination of the water phase is not negligible, since the composition of the salt rich phase in equilibrium with the ionic liquid rich phase is 22.00 wt % of  $K_3PO_4$  and 25.00 wt % of ionic liquid, thus leading to additional environmental problems. On the other hand, the fatty acid-based DESs here proposed are all immiscible with water, not requiring the addition of salting out agents, making them more economic and environmentally friendly. Since the proposed DESs present very low solubility in water, minimal cross contamination of the aqueous phase occurs, as can be seen by NMR spectra. It should be remarked that in this work the recovery of BPA from DESs has not been addressed; however, it can be easily recovered from the DES phase, by the addition of water as antisolvent and changes in pH, which lead to the pollutant precipitation and allow the DES reuse with minimal losses, as previously reported.<sup>39,40</sup>

It was demonstrated that the alternative process herein proposed is greener, safer, nontoxic, and more economical than ionic liquid-based aqueous biphasic systems and it illustrates the potential of the fatty acid DES solvents in the removal of persistent pollutants from water environments.

## CONCLUSIONS

In this work, new low viscous hydrophobic DESs containing only fatty acids, that can act as hydrogen bond donors and acceptors simultaneously, are presented and studied for the first time. These new solvents are eutectic mixtures composed of several fatty acids, namely octanoic, nonanoic, decanoic, and dodecanoic acids, in different proportions. These hydrophobic solvents were designed to be chemically stable when in contact with water environments, which was proved using NMR spectroscopy.

Densities and viscosities were studied in the range of temperatures from 20 to 80 °C, for dried and water saturated DESs. Contrary to common deep eutectic solvents, these new eutectic solvents presented the lowest viscosities ever obtained (2–14 mPa·s) for this class of solvents and densities lower than water, independently of the water content.

These new fatty acids based DESs have a privileged place among the green solvents, since they are immiscible in water and still have low viscosity. In addition, taking advantage of their hydrophobic character and the low viscosity, which allows quick and efficient mass transfer between the two phases in equilibrium, these DESs were used to extract one micro-pollutant, bisphenol A, from water, illustrating one of the major concerns of our society, clean water. Very high one-step extraction efficiencies (around 92%) were obtained for binary and ternary fatty acid-based DESs, showing that it is possible to tune the extraction efficiencies by introducing new components into the DESs.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b04235.

Experimental data of thermal properties, density and viscosity of dried and water saturated fatty acid-based

DESs studied in this work; the fitted density and viscosity for the studied DES; and finally, the characterization of DESs using NMR spectroscopy, as well as the NMR spectra of the water-rich phase after the extraction experiments using these DES (PDF)

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### Notes

The authors declare no competing financial interest.

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