Article

Structure-Physical Properties Relationship of Eutectic Solvents Prepared from Benzyltriethylammonium Chloride and Carboxylic Acids

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Deep eutectic solvents (DESs) have attracted the attention of the researchers as alternative solvents due to desirable properties such as easy preparation and high thermal stability. In this work, it was reported the preparation of five DESs from benzyltriethylammonium chloride (BTEAC) as quaternary ammonium salt (QAS) and carboxylic acids (oxalic, malonic or benzoic) as hydrogen bonding donor (HBD), which four were not reported so far. Furthermore, it was presented the first type III liquid DES at room temperature from benzoic acid and shown by interaction energy calculations why the formation of benzyltriethylammonium chloride:benzoic acid (BTEAC:BA) is favored over choline chloride:benzoic acid (ChCl:BA). The optimized geometries showed the Cl···π interaction is determining for decreasing the freezing point of benzyltriethylammonium chloride:benzoic acid mixture. Infrared spectra showed evidence for the existence of hydrogen bonds in DESs. Physical (freezing point, density and refractive index), thermal (thermogravimetric analysis) and rheological characterizations were performed for all solvents. The structure of HBDs affected the results on all evaluated properties and proved that it could be tunable. The prepared DESs were stable thermically and can be used in a wide range of temperature. Finally, rheological studies showed that Newtonian or non-Newtonian behavior can be observed by the nature of HBD.

Keywords: deep eutectic solvents, benzyltriethylammonium chloride, carboxylic acids, physical properties

Introduction

Deep eutectic solvents (DESs) are eutectic mixtures prepared at a specific molar ratio and have a lower eutectic point than the ideal liquid mixture.[1,2] Basically, the general formula for DES is Cat^+X^- zY, and they are divided into five classes:[1,3]

$$\text{Type I: } Cat^+X^- \ zMCl_x \qquad (1)$$
$$\text{Type II: } Cat^+X^- \ zMCl_x \ . yH_2O \qquad (2)$$
$$\text{Type III: } Cat^+X^- \ zRZ \qquad (3)$$

$$\text{Type IV: } MCl_x + RZ \qquad (4)$$
$$\text{Type V: non-ionic DES} \qquad (5)$$

where Cat^+: organic cations (usually ammonium or phosphonium); X^-: Lewis base (normally halide); Y: Lewis or Bronsted acid; z: number of Y molecules; M: metal; R: alkyl or aryl; $Z = -OH, -COOH, -CONH_2$.

Type III DESs have been applied in multicomponent reactions, food analysis, the capture of toxic gases, extractive desulfurization of fuel oil, pharmaceutical formulation, drug delivery, synthesis and dissolution of metal oxides.[1,2,4-7] The quaternarium ammonium salt (QAS) most studied in scientific works is the choline chloride

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(ChCl) due to physical (highly soluble in water), chemical (formation of DESs with various types of hydrogen bonding donors (HBDs)) and economical (low price and high availability) aspects.[2] Carboxylic acids have been widely used as HBDs in the preparation of type III DESs with specific properties.[8-11] In 2014, Florindo *et al.*[8] prepared DESs from ChCl and carboxylic acids (levulinic, glutaric, malonic, oxalic, and glycolic) to evaluate the influence of HBDs in the thermophysical properties. Density, viscosity, and refractive index were affected by the nature of the HBD and proved that molar ratio variation or structural changes in HBD allowed the preparation of a range of DESs with tunable properties.[8] Moreover, DESs prepared from malonic, anhydrous or hydrated oxalic acid as HBD and choline chloride as QAS has been applied in the pretreatment, extraction, catalysis of biomass and food waste and the results show environmental and economic benefits.[1] In this context, the preparation of new type III DESs from carboxylic acids and quaternary ammonium salts can contribute to improving the results in the mentioned areas.

Benzyltriethylammonium chloride (BTEAC) is a cationic surfactant and have been applied in electrochemistry, photochemistry, agent decontaminant and as a phase-transfer catalyst in organic synthesis.[12-17] Although BTEAC is used for several applications, it as QAS was under-explored to date in the preparation of type III DESs. In 2017, Taysun *et al.*[18] tested the effect of HBDs with one, two or three acidic groups (*p*-toluenesulfonic monohydrate, oxalic dihydrate, and citric monohydrate acids) on the density, refractive index, viscosity, conductivity, and pH of eutectic solvents prepared from BTEAC. The authors[18] pointed out that BTEAC:citric acid monohydrate (1:1) provided a very high viscosity, which hampered the handling and the determination of density and viscosity. Recently, DESs have been used successfully as a solvent in the synthesis of 1,2,4-triazolo[1,5-*a*]pyrimidines and 4-acyl-1-substituted-1,2,3-triazoles.[19,20] In the continuation of our studies, the limited number of DESs prepared from BTEAC and HBDs associated with the importance of designing new solvents with tunable properties motivated us to evaluate these systems. In this work, it was chosen only mono and dicarboxylic acids (benzoic (BA), malonic (MA), and oxalic acid (OA)) as HBDs and proposed the preparation and physical (freezing point, density and refractive index), thermal (thermogravimetric analysis), and rheological characterization of DESs from these acids and BTEAC as QAS. Five DESs were prepared, which four were not reported so far. Our goal was to study the impact of the structure of HBDs on the physical properties of DESs. Furthermore, infrared 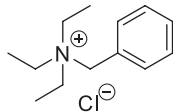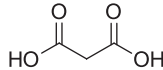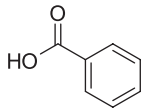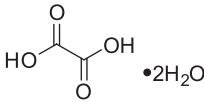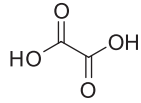(IR) spectroscopy was used to compare the spectra of DESs with their individual components. Finally, quantum chemical calculations were performed to generate insights about the interactions in the formation of liquid deep eutectic solvents with benzoic acid.

Experimental

Materials

All reagents were purchased from Sigma-Aldrich (Milwaukee, USA) with a stated purity of 99%. All chemicals were dried under vacuum for 48 h and used in the preparation of DESs as supplied without further purification. All details about the chemicals used in this work are given in Table 1.

Table 1. Name, structure and CAS number of chemicals used in this work

Chemical name	Structure	CAS number
Benzyltriethylammonium chloride		56-37-1
Malonic acid		141-82-2
Benzoic acid		65-85-0
Oxalic acid dihydrate		6153-56-6
Oxalic acid		144-62-7

Preparation of DESs

BTEAC (11.388 g, 50 mmol) and acid (1:1 or 1:2 molar ratio) were added into a round bottom flask. The mixture was heated at 100 °C and stirred for 15 min for malonic acid and 1 h for oxalic and benzoic acids.[8,10] Figure S1 (Supplementary Information (SI) section) shows the acronyms, molar ratios, and apparency of DESs prepared in this work.

Methods

Quantum chemical calculations were performed with the ORCA 4.2.0 program package.[21,22] The structures

of the benzoic acid, QASs (ChCl and BTEAC), and DESs (BTEAC:BA and ChCl:BA) were optimized at the ωB97X-D3/cc-pVDZ level of theory. The starting geometries of DESs were generated from previously optimized geometries of benzoic acid and QASs. Harmonic frequencies were calculated to ensure that all optimized structures are minima in potential energy. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance II 400 (^{1}H at 399.01 MHz and ^{13}C at 100.33 MHz) at 45 °C in a 5 mm sample tubes in dimethyl sulfoxide/tetramethylsilane (DMSO-d_6/TMS) solutions (digital resolution ± 0.01 ppm). ^{35}Cl NMR experiments were recorded on a Bruker Avance II 400 (^{35}Cl at 39.14 MHz) at 45 °C in 5 mm sample tubes in DMSO-d_6 using KClO$_4$ as standard. Infrared spectra were recorded on a Jasco FT-IR 4100 spectrophotometer in the 4000-400 cm^{-1} region at room temperature. Thermogravimetric analysis (TGA) was carried out using a TGA STA449 F3 Jupiter® instrument (NETZSCH, Gerätebau GmbH, Germany) calibrated by CaC$_2$O$_4$.H$_2$O (99.9%). 5-10 mg of samples were placed in an open α-alumina pan and heated at a rate of 10 °C min^{-1} from 30 to 500 °C. All measurements were recorded under a nitrogen atmosphere with a flow rate of 50 mL min^{-1}. Rheological properties were analyzed using an Anton Parr MCR 72 (Modular Compact Rheometer) using parallel plate PP25 geometry (25 mm diameter; 0.50 mm gap). Steady shear measurements were performed at a constant temperature of 25 °C and at 0.1-1000 s^{-1} shear rate, which was plotted on a 30-point graph for each eutectic solvent. Viscosity as a function of temperature was measured in the range of 20-130 °C at 50 s^{-1} shear rate. The equipment has temperature control and the accuracy indicated by the manufacturer is ± 0.5 °C and a precision of ± 0.01 Pa s for the measured value. Densities were determined at 25 °C using a 10 mL pycnometer. Experiments were performed in triplicate, and the density value is a result of this average. The chemicals were weighed using a Shimadzu AUY 220 balance with a precision of ± 10^{-4} g. Freezing points were determined by the cooling DESs sample in an ice bath. A Clink CK-2769 digital thermometer with a precision of ± 0.1 °C was inserted into the vial containing the eutectic solvent for temperature control. Experiments were performed in triplicate, and the freezing point is a result of this average. The refractive indexes were obtained by an Atago automatic digital refractometer (model RX-7000α) with a resolution of ± 10^{-5} and 0.01 °C for the refractive index and temperature, respectively. The refractometer was calibrated with distilled water at 20 °C and the measurements were performed from 20 to 70 °C. Experiments were performed in triplicate, and the refractive index is a result of this average.

Results

Preparation of DESs

Initially, four eutectic solvents were prepared from BTEAC and oxalic acid dihydrate, oxalic acid, malonic acid and benzoic acid at a 1:1 molar ratio to evaluate the effect of HBDs structure on physical properties. Afterward, a DES was prepared from BTEAC and malonic acid at a 1:2 molar ratio to compare its physical properties to the 1:1 mixture (Table 2).

Table 2. Acronyms, molar ratio and apparency of DESs prepared in this work

Acronym	Molar ratio	Apparency
BTEAC:OA•2H$_2$O^a	1:1	transparent liquid
BTEAC:OA^b	1:1	transparent liquid
BTEAC:BA^b	1:1	transparent viscous liquid
BTEAC:MA^b	1:1	transparent liquid
BTEAC:MA^b	1:2	transparent liquid

^{a}Previously reported in reference 18; ^{b}new eutectic solvents. BTEAC: benzyltriethylammonium chloride; OA: oxalic acid; BA: benzoic acid; MA: malonic acid.

Spectroscopic data

Nuclear magnetic resonance (^{1}H, ^{13}C, and ^{35}Cl nucleus) and infrared spectroscopies were performed for all DESs (Figures S3-S23, SI section). Table 3 shows the characteristic infrared stretches of DESs and their HBDs.

Freezing point

Table 4 shows the values determined for DESs freezing points (fp$_{DES}$) and calculated for the difference between the QAS freezing point (fp$_{QAS}$, °C) and DES freezing point (fp$_{DES}$, °C), which were called Δfp. The formula used to calculate Δfp was:

$$\Delta fp = fp_{QAS} - fp_{DES} \tag{6}$$

In this work, freezing points of DESs prepared from BTEAC (entries 1, 2, 4, 6, and 8, Table 4) ranged from −3 to 11 °C. These results were compared to freezing points of DESs prepared from ChCl by Abbott *et al.*,[10] which ranged from 10 to 95 °C (entries 3, 5, and 7, Table 4).

Quantum chemical calculations

Quantum mechanical calculations were performed to provide energy data at the ωB97X-D3/cc-pVDZ level

Table 3. Selected infrared frequencies from eutectic solvents and their HBDs

entry	Compound	C=O / cm^{-1}	O–H band / cm^{-1}	C–O / cm^{-1}
1	OA	1685	3700-3100 (br)	1255
2	BTEAC:OA (1:1)	1741	3700-3065 (br)	1240
3	OA•2H$_2$O	1688	3700-3170 (br)	1254
4	BTEAC:OA•2H$_2$O (1:1)	1746	3700-3070 (br)	1244
5	BA	1687	3300-2559 (br)	1292
6	BTEAC:BA (1:1)	1708	3600-2530 (br)	1267
7	MA	1728	3600-3100 (br)	1314
8	BTEAC:MA (1:1)	1719	3500-3100 (br)	1330
9	BTEAC:MA (1:2)	1725	3700-3200 (br)	1317

OA: oxalic acid; br: broad; BTEAC: benzyltriethylammonium chloride; BA: benzoic acid; MA: malonic acid.

Table 4. Freezing points of DESs based on ChCl or BTEAC and carboxylic acids

entry	DES	fp$_{DES}$^{a} / °C	Δfp / °C	Reference
1	BTEAC:OA•2H$_2$O (1:1)	6.0 ± 0.6	184	this work
2	BTEAC:OA (1:1)	9.2 ± 0.5	181	this work
3	ChCl:OA (1:1)	34	268	10
4	BTEAC:MA (1:1)	9.9 ± 0.7	180	this work
5	ChCl:MA (1:1)	10	292	10
6	BTEAC:BA (1:1)	11.4 ± 0.7	179	this work
7	ChCl:BA (1:1)	95	207	10
8	BTEAC:MA (1:2)	−3.3 ± 0.7	193	this work

^{a}Standard deviation values are indicated for each eutectic solvent. DES: deep eutectic solvent; fp$_{DES}$: DES freezing point; Δfp: difference between the quaternary ammonium salt (QAS) freezing point (fp$_{QAS}$) and DES freezing point (fp$_{DES}$); BTEAC: benzyltriethylammonium chloride; OA: oxalic acid; ChCl: choline chloride; MA: malonic acid; BA: benzoic acid.

of theory, aiming insights about the interaction between HBD and QAS in the formation of DESs. Due to its good performance in many applications, the ωB97X-D3 method was chosen, including the analysis of bonded and non-bonded interactions.[23,24] The cc-pVDZ basis set was used by its good relationship between computational cost and accurate results. The optimized geometries (Figure S2), the atomic coordinates for ChCl:BA (Table S1), and BTEAC:BA (Table S2) and the DESs intermolecular interactions energies (Table S3) are shown in the SI section.

Thermogravimetric analysis

The temperature at which there was a loss of 10% of the mass of the compound (T$_{onset (10\%)}$), the maximum of the derivative thermogravimetry (DTG) curve (T$_d$), and the final decomposition temperature (T$_f$) obtained for DESs are shown in Table 5. The thermograms of BTEAC, HBDs, and DESs are shown in Figures S24-S32 in the SI section.

Density

Table 6 presents the density of pure HBDs (ρ HBD) given by the supplier, as well as the density of DESs

Table 5. T$_{onset (10\%)}$, T$_d$ and T$_f$ of BTEAC, HBDs, and DESs

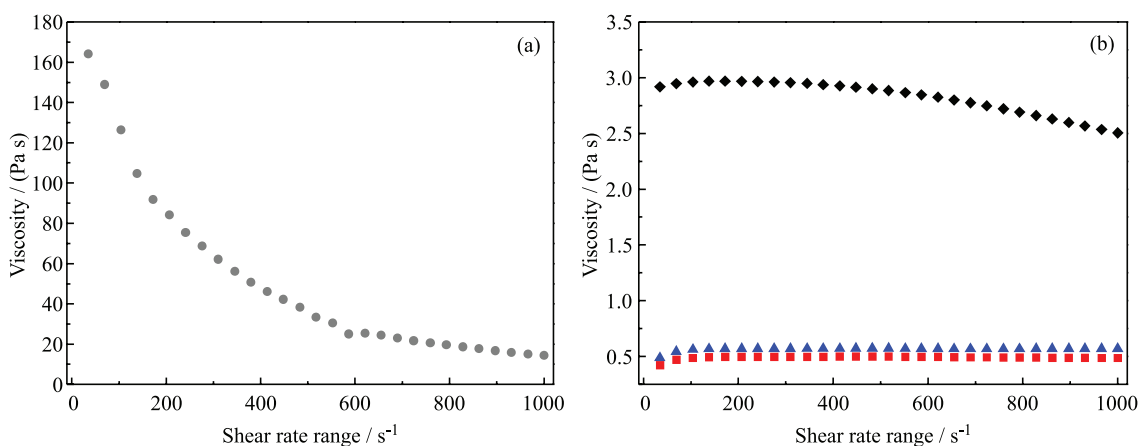| Compound	T$_{onset (10\%)}$^{a} / °C	T$_d$^{b} / °C	T$_f$^{c} / °C
BTEAC	197	202	225
OA•2H$_2$O	71	86/179	190
OA	152	186	200
BA	137	178	185
MA	159	177	193
BTEAC:OA•2H$_2$O (1:1)	160	212	232
BTEAC:OA (1:1)	182	209	235
BTEAC:BA (1:1)	172	202	225
BTEAC:MA (1:1)	148	197	230
BTEAC:MA (1:2)	126	136/196	225

^{a}T$_{onset (10\%)}$ is the temperature at which there was a loss of 10% of the mass of the compound; ^{b}T$_d$ is the maximum of the DTG curve; ^{c}T$_f$ is the temperature of total decomposition. BTEAC: benzyltriethylammonium chloride; OA: oxalic acid; BA: benzoic acid; MA: malonic acid.

(ρ DES) and the molar mass (MM DES) determined in this work. According to the literature,[25] DESs are mixtures, and the average molar mass (MM) is calculated using the following formula: x$_1$MM$_1$ + x$_2$MM$_2$, where x is the molar fraction and MM is the molar mass of each component.

Table 6. Experimental densities of HBDs and DESs at 25 °C and molar mass of DESs

entry	DES	ρ HBD[a] / (g cm⁻³)	ρ DES[b] / (g cm⁻³)	MM DES / (g mol⁻¹)
1	BTEAC:OA (1:1)	1.90	1.1854 ± 0.0009	158.90
2	BTEAC:OA•2H₂O (1:1)	1.65	1.1729 ± 0.0010	176.92
3	BTEAC:MA (1:1)	1.60	1.1154 ± 0.0013	165.91
4	BTEAC:BA (1:1)	1.32	1.0933 ± 0.0016	174.94
5	BTEAC:MA (1:2)	1.60	1.1762 ± 0.0012	145.29

[a]Values were given by the supplier; [b]standard deviation values are indicated for each eutectic solvent. ρ HBD: density of hydrogen bonding donor; ρ DES: density of deep eutectic solvent; MM DES: molar mass of deep eutectic solvent; BTEAC: benzyltriethylammonium chloride; OA: oxalic acid; MA: malonic acid; BA: benzoic acid.

Figure 1. Viscosity *vs*. shear rate for (a) BTEAC:BA (1:1) (●) at 25 °C and (b) BTEAC:OA•2H₂O (1:1) (◆), BTEAC:MA (1:1) (■) and BTEAC:MA (1:2) (▲) at 25 °C.

Rheological behavior

Figure 1 shows the viscosity (Pa s) as a function of shear rate (s⁻¹) at 25 °C for all DESs prepared. Tables S4-S7 (SI section) show the values of shear rate, shear stress, viscosity, and torque obtained for all DESs. Table S8 (SI section) shows the values of temperature, shear stress, viscosity, and torque obtained for BTEAC:BA (1:1).

Refractive index

Table 7 presents the refractive index (n) values at 25 °C of eutectic solvents prepared from BTEAC. Table S9 (SI section) shows the refractive indexes as a function of temperature from 20 to 70 °C.

Discussion

Fourier transform infrared (FTIR) analysis was performed for BTEAC, HBDs, and DESs to identify the functional groups and the presence of hydrogen bonds in DESs. The peaks assigned to BTEAC were (in cm⁻¹): =C−H sp² (3071 and 3020), C−H sp³ (2984), C−N (1156), C=C$_{arom}$ (1497 and 1484), −CH₃ bend (1372) and −CH₂

Table 7. Refractive index (n) values at 25 °C of DESs prepared from BTEAC

entry	DES	Refractive index (n)
1	BTEAC:OA•2H₂O (1:1)	1.50992
2	BTEAC:OA (1:1)	1.52088
3	BTEAC:BA (1:1)	1.55977
4	BTEAC:MA (1:1)	1.53210
5	BTEAC:MA (1:2)	1.50904

DES: deep eutectic solvent; BTEAC: benzyltriethylammonium chloride; OA: oxalic acid; BA: benzoic acid; MA: malonic acid.

bend (1453), C−H$_{arom}$ wagging (756 and 713). IR spectra of all DESs did not show differences in the vibrational wavenumbers attributed to BTEAC compared to the pure BTEAC spectrum, as illustrated by the BTEAC and BTEAC:BA (1:1) overlapped spectra (Figure S18, SI section). This indicates that the cationic fragment of BTEAC does not interact with HBDs when DESs are formed. Such information evidence that shifts are associated with hydrogen bonding between the anion (Cl⁻) and HBD. Figures S19-S23 (SI section) show the overlapping of DESs and their HBDs infrared spectra. DESs prepared from oxalic acid anhydrous, oxalic acid dihydrate,

and benzoic acid display higher wavenumber shifts for C=O stretch and lower C−O stretch wavenumber shifts compared to their HBDs. The O−H band was shifted to lower wavenumber in all these cases (entries 1-6, Table 3). Eutectic solvents prepared from malonic acid (1:1 and 1:2) slightly change the C=O and C−O stretches to lower wavenumber compared to malonic acid. Regarding the O−H band, BTEAC:MA (1:1) shows lower wavenumber shift, whereas BTEAC:MA (1:2) shows higher wavenumber compared to neat malonic acid (entries 7-9, Table 3). In the resume, the frequencies assigned to C=O, C−O stretches, and O−H band of DESs was moved to higher or lower values compared to the respective HBDs wavenumbers (Table 3) in line with previously reported works.[15-17,26-28] The ^{1}H NMR analysis indicates the presence of BTEAC signals at 1.31 ppm (triplet, −CH$_3$), 3.24 ppm (quartet, −CH$_2$N), 4.56 ppm (singlet, −CH$_2$Ph), 7.48-7.60 ppm (multiplet, -phenyl) and seven signals in the ^{13}C NMR at 7.2 (−CH$_3$), 52.4 (−CH$_2$N), 60.1 (−CH$_2$Ph), 127.3, 129.3, 130.7 and 132.5 ppm (phenyl) in all eutectic solvents. The other chemical shifts were signed to the HBDs present in the DESs (δ, ppm): 160.9 (carbonyl carbon in oxalic acid); 161.7 (carbonyl carbon in oxalic acid dehydrate); 41.8 and 167.9 (methylene and carbonyl carbon in malonic acid, respectively); 128.2, 128.8, 129.9, 132.4, 166.9 (aromatic carbons in benzoic acid). Regarding the ^{35}Cl NMR experiments, the literature[29,30] presents a few articles in which the chemical shift for the chloride ion was determined in eutectic solvents. The chemical shifts were similar in all DESs and ranged from −2.72 to −3.58 ppm, which are close to the chemical shift of the chloride ion from BTEAC (−2.39 ppm).

Liquid DESs at room temperature prepared from oxalic acid (ChCl:OA 1:1; tetrabutylammonium bromide (TBAB):OA 1:1) and malonic acid (ChCl:MA 1:1 and 1:2; TBAB:MA 1:1) are well known.[8,10,11] On the other hand, to the best of our knowledge, type III liquid DESs at room temperature were not prepared from benzoic acid. For example, the mixtures ChCl:BA (1:1) and trimethylglycine:BA (1:2) presented freezing points of 95 and 53 °C, respectively.[9,10] Thus, BTEAC:BA (1:1) is the first type III liquid DES at room temperature prepared from benzoic acid. Benzoic acid is used as food preservatives due to the inhibition of fungi, yeasts, and some bacteria.[31] Moreover, benzoic acid and their derivates are used in medicine and cosmetic formulations.[32-34] Due to these applications, the design of new eutectic solvents from benzoic acid is a significant contribution to the area. This result led us to the first question: why is BTEAC:BA (1:1) liquid at room temperature? The first work on type III eutectic solvents reported by Abbott *et al.*[29] showed two key patterns

concerning the cationic fragment of the QAS: (*i*) as cation symmetry decreases, the freezing point of the DES decreases; (*ii*) the presence of groups capable of performing stronger intermolecular interactions (hydrogen bond or dipole-dipole) with HBD favored the reduction of freezing point compared to groups performing London or π-π interactions. In the case of BTEAC:BA (1:1), the non-symmetry of QAS could lead to the formation of liquid DES with benzoic acid. However, the second trend does not favor our result, since BTEAC does not have polar groups. The second trend observed by Abbott *et al.*[29] led to a second question: if polar groups often favor the reduction of freezing points, why do other salts such as ChCl not form liquid mixtures with benzoic acid? More recent works[35,36] have attempted to explain the formation of eutectic solvents by theoretical calculations for intermolecular interactions. Therefore, our first goal was to study why liquid DES with benzoic acid was formed only when BTEAC was used. The pharmacological importance of benzoic acid and the fact that BTEAC:BA (1:1) is the first liquid DES at room temperature prepared from benzoic acid motivated us to investigate why the formation of BTEAC:BA (1:1) is favored to ChCl:BA (1:1). Thus, quantum mechanical calculations were performed to provide energy data at the ωB97X-D3/cc-pVDZ level of theory to achieve insights about the interaction between HBD and QAS in the formation of DES. The DESs optimized geometries (Figure S2, SI section) showed that in both cases, BA interacts preferably with the chloride ion of the QAS. In ChCl:BA, the Cl···HO interaction (distances of 2.119 Å for Cl···H and 3.045 Å for Cl···O) is preferred, whereas the Cl···π interaction (a distance of 3.493 Å between Cl and the *ortho* carbon of phenyl) is favored in BTEAC:BA.

The freezing point of a substance is directly correlated with the strength of the intermolecular interactions present in its structure.[37] Thereby, the lower the intermolecular interaction strength lower will be its freezing point. The calculated intermolecular interaction energies (Table S3, SI section) showed that the total interaction energy (ΔE_{INT}) is lower for BTEAC:BA (−122.72 kcal mol^{-1}) than for the ChCl:BA (−140.54 kcal mol^{-1}) and therefore a lower freezing point is expected for the first one. This finding is corroborated by the data obtained for the $E_{BA\cdots QAS}$ energy (Table S3), which showed that BA interacts more strongly with the BTEAC chloride ion (−29.90 kcal mol^{-1}) than the ChCl one (−24.35 kcal mol^{-1}). This weakens the coulombic attraction between cation and anion within BTEAC, decreasing the total intermolecular interaction energy and freezing point.

Applicability of solvents depends on the range of temperatures they remain liquids. Determination of

freezing point (fp) and thermogravimetric analysis (TGA) give the temperature the DESs solidificate and evaporate or decompose, respectively. The freezing point can be determined by cooling DESs in an ice bath or similar procedures.[18,38] Based on the results shown in Table 4, the standard deviation ranged from 0.5-0.7 °C, which shows that the procedure was accurate. Also, trends were observed in our results compared to data published by Abbott *et al.*[29] for DESs prepared from ChCl (Table 4). The freezing points of BTEAC and ChCl are 190 and 302 °C, respectively. Comparison between the values of Δfp in entries 2 and 3 (181 and 268 °C) or 4 and 5 (180 and 292 °C) shows that the interaction between ChCl and oxalic or malonic acid decreases the freezing points more sharply than the interaction between BTEAC and the same HBDs. The difference between the values of Δfp from entries 2 and 3 in Table 4 is 87 °C whereas the difference between Δfp from entries 4 and 5 in Table 4 is 112 °C. However, Δfp is similar for BTEAC:BA (179 °C, entry 6, Table 4) and ChCl:BA (207 °C, entry 7, Table 4). In this case, the difference between the Δfp is only 28 °C.

The thermogravimetric analysis allows determining the maximum of the DTG curve (T_d), final decomposition temperature (T_f), and 10% weight loss ($T_{onset\ (10\%)}$) of a sample. These data are important for new DESs characterization and determine the applicability. As expected, the values of $T_{onset\ (10\%)}$, T_d, and T_f obtained for our DESs are different from those obtained for both BTEAC and HBDs (Table 5). The values determined for $T_{onset\ (10\%)}$ shows that BTEAC:OA•$2H_2O$, BTEAC:OA, and BTEAC:BA are less stable (160, 182 and 172 °C, respectively) than BTEAC (197 °C), however, more stable than HBDs (71, 152 and 137 °C, respectively), whereas BTEAC:MA (1:1 and 1:2) are both less stable (148 and 126 °C, respectively) than BTEAC and MA (197 and 159 °C, respectively). The order of stability of the DESs prepared in this work is: BTEAC:OA > BTEAC:BA > BTEAC:OA•$2H_2O$ > BTEAC:MA (1:1) > BTEAC:MA (1:2). The presence of water of hydration in BTEAC:OA•$2H_2O$ decreases the thermal stability comparing to BTEAC:OA. Furthermore, a thermally stable HBD did not result in greater stability of DESs. For example, malonic acid was the most stable HBD, whereas DES prepared from it was less stable. Moreover, the increased molar ratio of malonic acid decreased the thermal stability of DES. Regarding the T_d values of the starting materials, BTEAC (202 °C), OA (186 °C), BA (178 °C) and MA (177 °C) presented only one decomposition step whereas OA•$2H_2O$ exhibited two steps (86 and 179 °C). All eutectic solvents with a 1:1 molar ratio (BTEAC:OA•$2H_2O$, BTEAC:OA, BTEAC:BA, BTEAC:MA) showed one decomposition

step. However, the values are different from their starting materials (212, 209, 202, and 197 °C, respectively). In addition, BTEAC:MA (1:2) presented two decomposition steps (136 and 196 °C), which are different from neat BTEAC or malonic acid. T_{onset} and T_d confirm that DESs thermal behavior is unique and differs from its components. All our DESs completely decompose between 190 and 235 °C, according to the T_f values shown in Table 5. The association of freezing point and TGA data allows to say that all eutectic solvents of this work can be used at temperatures between 11 and 125 °C without solidification or decomposition.

Density and viscosity are important to determine the flow behavior of a solvent.[18] Density is an important property in simple procedures such as small scale extractions but also in more complicated applications such as the design for technical applications of new chemical adsorbents.[39] The value of the density (d) is determined by mass (m) to volume (V) ratio: $d = m / V$. Essentially, the density can be affected by four main factors: temperature, pressure, intermolecular interactions and molar mass.[40] Concerning density, three main trends have been observed in DESs prepared from BTEAC: (*i*) HBD structure directly affects density; (*ii*) DESs prepared from HBDs containing two carboxylic acid functions present higher densities; (*iii*) density increases when the HBD molar ratio increases. The densities of DESs in the 1:1 molar ratio showed the order BTEAC:OA > BTEAC:OA•$2H_2O$ > BTEAC:MA > BTEAC:BA which coincided with the density order of the respective pure HBDs (OA > OA•$2H_2O$ > MA > BA) (entries 1-4, Table 6), confirming the first trend. Intermolecular interactions strongly influenced the densities in accordance with trend two. Oxalic acid only performs hydrogen bond interactions, therefore, BTEAC:OA presented the highest density value (1.1854, entry 1, Table 6). Using oxalic acid dihydrate as HBD decreased the density (1.1729, entry 2, Table 6). This effect has already been reported in the literature[8] for other DESs. A spacer group (−CH_2) between the carbonyls significantly decreased the density value, as observed for BTEAC:MA (1.1154, entry 3, Table 6). Probably, the addition of this spacer group alters the supramolecular arrangement of the eutectic solvent allowing London interactions (weaker than hydrogen bonds). These weaker interactions leave the molecules more dispersed and decrease the density. The value obtained for BTEAC:BA (1:1) was the lowest one (1.0933, entry 4, Table 6) because benzoic acid presents only one carboxyl group to make hydrogen bonds whereas malonic and oxalic acids present two carboxyl groups. The third trend was followed by the DESs obtained from malonic acid in 1:1 and 1:2 molar

ratios (1.1154 and 1.1762, entries 3 and 5, Table 6). A higher density was measured for BTEAC:MA (1:2) due to the increased number of hydrogen bonds which improve the molecular cohesion. The standard deviation values for density ranged from 0.0009-0.0016 g cm^{-3}. These results indicate that our measurements were accurate and are in accordance with the values already determined for DESs in the literature.[8,18,26,38,41]

Viscosity measurements as a function of shear rate determine whether the substance presented Newtonian or non-Newtonian behavior. Newtonian fluids show constant viscosity behavior over the change in shear or external force. On the other hand, non-Newtonian change viscosity as a function of the shear rate.[42] Non-Newtonian fluids are subdivided in dilatant or pseudoplastic. The difference between dilatant and pseudoplastic fluids is that the viscosity of the first increases while the viscosity of the second decreases when the shear rate increases. In this sense, Newtonian fluids can be associated with polymers to improve flow behavior.[43] On the other hand, non-Newtonian fluids can be applied in lubricants, printing technology, damping and braking devices, personal protective equipment, mechanical processing.[44,45] In the case of pseudoplastic fluids, it can be used in water-based paints, medical injection or energy transport fields.[46,47] Knowing DESs rheological properties is important to define their applications. However, our literature search found only three works[48-50] that discuss viscosity as a function of shear rate for DESs containing carboxylic acids as HBDs combined with ChCl and benzyltripropylammonium chloride (BTPAC). Accordingly, this is the first work that discusses the rheological behavior for DESs obtained from BTEAC and carboxylic acids (OA, MA and BA). The nature of the HBD strongly influenced the results since both behaviors (Newtonian and non-Newtonian) were observed for our DESs prepared from BTEAC and carboxylic acids. BTEAC:BA showed a pseudoplastic non-Newtonian behavior (Figure 1a). In contrast, the DESs containing oxalic or malonic acids as HBD exhibited Newtonian behavior (Figure 1b). Concerning viscosity, BTEAC:OA•2H$_2$O (1:1), BTEAC:MA (1:1) and BTEAC:MA (1:2) presented values in the same order of magnitude (2.91, 0.42, and 0.48 Pa s at 34 s^{-1}, respectively), while BTEAC:BA (1:1) presented a higher value (164 Pa s at 34 s^{-1}). Considering the highest viscosity presented by BTEAC:BA (1:1), viscosity as a function of temperature measurements were performed (Figure S33, SI section). The viscosity decreased dramatically to ca. 18 Pa s at 40 °C, which makes handling this DES easier.

Refractive index is a specific property which can be used to determine the purity of substances.[18] The parameters that affect the refractive index are: temperature

(T), concentration, chemical nature, and incident light wavelength (λ).[40] The refractive indexes of DESs in the 1:1 molar ratio showed the order BTEAC:BA > BTEAC:MA > BTEAC:OA > BTEAC:OA•2H$_2$O (Table 7). The refractive index values (1.509-1.559) were significantly affected by the chemical structure of HBDs. DES prepared from oxalic acid dihydrate presented a lower refractive index than anhydrous form (1.50992 and 1.52088, entries 1 and 2, Table 7, respectively). In contrast, BTEAC:BA (1:1) presented higher refractive index value (1.55977, entries 3, Table 7) due to the aromatic ring of benzoic acid being polarizable.[25] BTEAC:MA in 1:1 molar ratio showed higher value (1.53210, entry 4, Table 7) compared to oxalic acid, however, lower than BTEAC:BA (1:1). Moreover, the refractive index decreased (1.53210 to 1.50904, entries 4 and 5, Table 7) when the molar ratio of HBD (malonic acid) was changed from 1:1 to 1:2 for BTEAC:MA. Regarding the standard deviation calculated for the refractive index, the values ranged from 0.00055-0.00152, which are in accordance with works reported in the literature.[18,51] The results of Table S9 (SI section) show that the refractive index values decreased at higher temperatures for all eutectic solvents. The increase in temperature causes thermal expansion and allows light rays to pass through the medium.[18,52] The literature[8,26] shows type III DESs prepared from carboxylic acids exhibited the same behavior.

Conclusions

It was reported herein the preparation of four new deep eutectic solvents from BTEAC and organic acids and evaluated the effect of HBD on structural, physical, and rheological properties. FTIR experiments showed frequency shifts for the C=O, C−O and O−H vibrations, in comparison to the pure BTEAC and HBDs FTIR spectra, which evidenced the hydrogen bonds formation in all eutectic solvents. Quantum chemical calculations gave insights to explain why BTEAC favored the formation of liquid DES at room temperature with benzoic acid, and the result corroborated with freezing point. The determination of freezing points and onset temperatures showed DESs prepared were stable thermally until 126 °C and can be used in a liquid state over a wide temperature range. The flow behavior study showed that the choice of HBD is a key factor for adjusting both density and viscosity of DESs. The refractive index was influenced by temperature, molar ratio, and structure of HBD. All these data help to understand the structural effects of HBDs on the physical properties of DESs and assist in the preparation of DES with tunable properties.

Supplementary Information

Supplementary information (DESs intermolecular interactions energies, optimized geometries of ChCl:BA and BTEAC:BA, atomic coordinates for optimized geometries of ChCl:BA (1:1) and BTEAC:BA (1:1), NMR and FTIR spectra, thermograms, viscosity data and refractive index as a function of temperature for all DESs) is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

Author Contributions

Guilherme C. Paveglio was responsible for conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, writing original draft, review and editing; Fernanda A. S. C. Milani for conceptualization, data curation, formal analysis, investigation, methodology, validation, visualization; André C. Sauer for conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing original draft; Alexandre R. Meyer for conceptualization, data curation, formal analysis, software, writing original draft; Daiane Roman for conceptualization, data curation, formal analysis, investigation, writing original draft; Lucas Pizzuti for conceptualization, formal analysis, funding acquisition, project administration, resources, supervision, writing original draft, review and editing.

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