



HAL
open science

New hydrophobic deep eutectic solvent for electrochemical applications

Nesrine Chaabene, Kieu Ngo, Mireille Turmine, Vincent Vivier

► **To cite this version:**

Nesrine Chaabene, Kieu Ngo, Mireille Turmine, Vincent Vivier. New hydrophobic deep eutectic solvent for electrochemical applications. *Journal of Molecular Liquids*, 2020, 319, pp.114198. 10.1016/j.molliq.2020.114198 . hal-02936182

HAL Id: hal-02936182

<https://hal.sorbonne-universite.fr/hal-02936182v1>

Submitted on 11 Sep 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

NEW HYDROPHOBIC DEEP EUTECTIC SOLVENT FOR ELECTROCHEMICAL APPLICATIONS

NESRINE CHAABENE, KIEU NGO, MIREILLE TURMINE, VINCENT VIVIER

Sorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, LISE,

F-75005 Paris, France

Abstract

Deep eutectic solvents (DESs) are known as cheap and biodegradable solvents which are easier to synthesize than ionic liquids (ILs). In this work, a new hydrophobic DES based on menthol is described. It consisted in a mixture of menthol and acetic acid in which ethanolamine has been added in order to increase the conductivity up to few $\text{mS}\cdot\text{cm}^{-1}$. The physicochemical properties as a function of temperature, in the range of 293 to 333 K, of this menthol-based DES have been compared to the ethaline, which is one of the most widely used DES. Cyclic voltammetry has been used to study the electrochemical behavior of an electroactive mediator, the hydroxymethylferrocene (FcMeOH), which is a reversible electrochemical system and its diffusion coefficient, determined in both DESs, is of the same order of magnitude than the one reported for the 1-ethyl-3-methylimidazolium bis(trifluoro-methanesulfonyl)imide (EMIMTFSI), which is the most widely used IL for electrochemical applications. This new class of DES thus provide an eco-friendly alternative for electrochemical applications.

Keywords: *menthol-based DES; hydrophobic solvent; biodegradable solvent; cyclic voltammetry*

Corresponding author:

Mireille Turmine: mireille.turmine@sorbonne-universite.fr

29 **1. Introduction**

30 With the emergence of green chemistry, ionic liquids (ILs) are currently used as an attractive
31 alternative to organic solvents [1, 2]. Despite their many interesting physicochemical properties
32 such as a low melting temperature ($< 100\text{ }^{\circ}\text{C}$), a high thermal stability, a low vapor pressure, a
33 non-flammability and a wide electrochemical potential window, ILs remain expensive and their
34 preparation can be relatively complex [3, 4]. Recently, deep eutectic solvents (DESs) have been
35 used as analogues and alternative green solvents to replace traditional solvents but also to take
36 advantage of some of the most prominent properties of ILs [5, 6]. They are generally composed
37 of at least two compounds bonded together by intermolecular forces such as hydrogen bonding.
38 These interactions result in a significant decrease in the melting point of the mixture, DESs
39 often becoming liquid at room temperature. Additionally, DESs have many advantages. For
40 example, they can be easily synthesized with a high purity at low cost, and their components
41 are biodegradable and have a low toxicity [7].

42 The first DESs described in the literature [8] are based on choline chloride and urea or ethylene
43 glycol, known as reline or ethaline, respectively. Even if choline chloride is one of the most
44 widespread components used for DESs [9-11], the presence of chloride may be a limiting factor
45 for applications in electrochemistry. Moreover, most of these choline-based DES media suffer
46 from their hydrophilicity. Interestingly, the almost unlimited number of possible combinations
47 offers an infinite range of DESs that can be custom-synthesized depending on the targeted
48 application [12] and it should also be mentioned that some DESs can be obtained by the mixing
49 of both ionic and non-ionic species.

50 Recently, the group of Marrucho [13, 14] has reported a new hydrophobic DES prepared from
51 menthol and an organic acid, which is used for the extraction of different biomolecules such as
52 caffeine, tryptophan, isophthalic acid, and vanillin from the aqueous phase to the eutectic
53 mixture phase. This new family of DESs should thus offer new perspectives for electrochemical
54 applications, but unfortunately these DESs have a poor ionic conductivity.

55 The main objective of this work is to investigate the preparation of a new DES based on the
56 mixture of menthol and carboxylic acid in which an amine has been added in order to increase
57 the conductivity up to few $\text{mS}\cdot\text{cm}^{-1}$, while still keeping the environmentally-friendly and bio-
58 compatible characters of the end solvent. Such a new hydrophobic DES should thus be a good
59 candidate as a new electrolyte for electrochemical applications.

60 First, the physicochemical properties of this DES including density, viscosity, conductivity and
61 electrochemical windows have been studied and compared to a usual DES (*i.e.* ethaline) and
62 common hydrophobic ionic liquid (*i.e.* EMIMTFSI). Then, its use as solvent for
63 electrochemical application has been investigated by cyclic voltammetry in presence of an
64 electroactive probe, namely the hydroxymethylferrocene (FcMeOH).

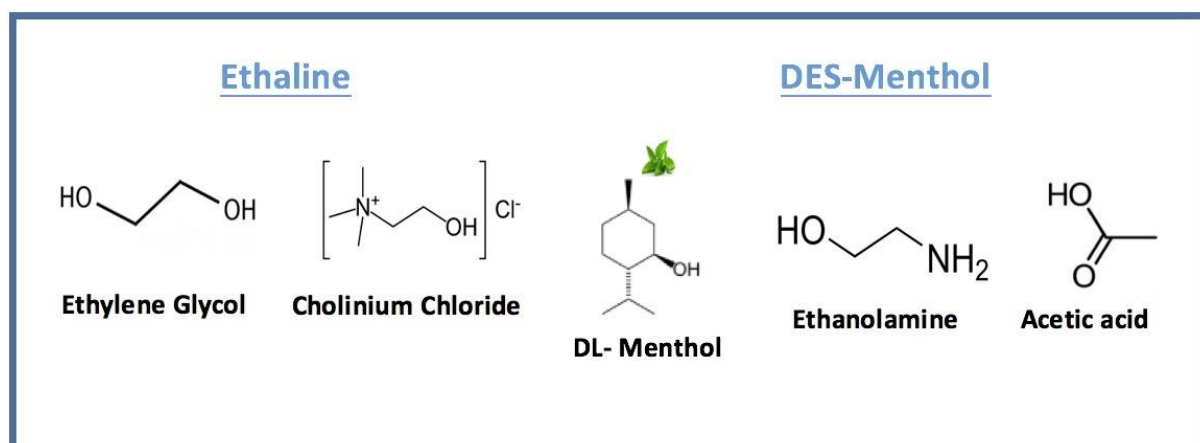
65

66 2. Experimental section

67 2.1 Chemicals and synthesis of DESs

68 Choline chloride (ChCl) (Acros Organics, purity $\geq 99\%$), ethylene glycol (EG) (VWR
69 Chemical, purity $\geq 99\%$), DL-Menthol (Sigma Aldrich, purity $\geq 95\%$), ethanolamine (Sigma
70 Aldrich, purity $\geq 98\%$) and acetic acid (Sigma Aldrich, purity $\geq 99.7\%$) were used as received.
71 The chemical structures of the compounds used for the synthesis of DESs are presented in Fig.
72 1.

73



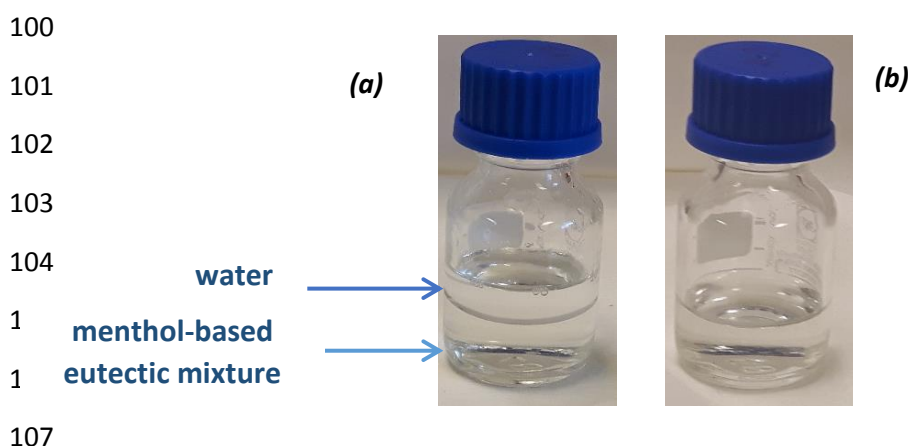
74

75 **Figure 1.** Chemical structures of the compounds used for the preparation of deep eutectic solvents
76 studied in this work.

77

78 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIMTFSI) was
79 synthesized according to the method previously described in the literature [15]. Its structure
80 was checked by ¹H NMR spectroscopy and ElectroSpray mass spectroscopy. ¹H NMR
81 spectroscopy (400 MHz, CDCl₃, δ /ppm relative to TMS), δ = 8.60 (s, 1H), 7.41(d, 2H, $J=10.3$),
82 4.25 (q, 2H, $J=7.36$), 3.93(s, 3H), 1.54(t, 3H, $J=7.4$). ElectroSpray mass spectroscopy (ESI
83 positive): m/z = 111.1 (EMIM⁺); (ESI negative) m/z = 280.1 (TFSI⁻). The estimated purity is
84 about 99%.

85 Ethaline was prepared by mixing cholinium chloride with ethylene glycol with a 1:2 molar
86 ratio. The mixture was stirred for 3 hours at room temperature to yield a homogeneous and
87 transparent liquid. The menthol-based eutectic mixture was prepared by mixing menthol,
88 ethanolamine and acetic acid in a 1:2:4 molar ratio. The mixture of these three compounds was
89 then heated at 80 °C for 30 min and then slowly cooled down until reaching room temperature
90 leading to a homogeneous transparent liquid. The water content in the three freshly prepared
91 solvent was titrated using a Karl – Fisher coulometer (C20, Mettler Toledo). Thus, the water
92 content of the hydrophobic ionic liquid (EMIMTFSI) was 50 ppm, that of menthol-based DES
93 was 85 ppm while the amount of water in ethaline was about 2000 ppm.
94 The hydrophobicity test was performed in order to characterize the role of menthol (Fig. 2) by
95 comparing two mixtures. The first one was a mixture of ethanolamine and acetic acid in a 2:4
96 molar ratio. The second mixture was the as-prepared menthol-based eutectic solvent. The same
97 amount of water (5 mL) was mixed with both mixtures, which resulted in the formation of two
98 phases in the case of the menthol-based eutectic mixture (Fig. 2a), whereas the acetic acid –
99 ethanolamine mixture mixed up with water (Fig. 2b).



108 **Figure 2:** *Hydrophobicity test for menthol-based eutectic solvent (a), and acetic acid – ethanolamine*
109 *mixture (b)*

112 2.2 Physicochemical characterization of the solvents

113 The density, viscosity and ionic conductivity of all the solvents were measured using the devices
114 listed in Table 1, in which the estimation of the average uncertainty for each physicochemical
115 property is also reported.

118

119

Table 1. *Device and uncertainty for physical-chemical property measurements*

Physicochemical property	Measurement device	Standard uncertainty
Density	Anton Paar DMA 5000	Less than 0.05 kg m ⁻³
Viscosity	Anton Paar Lovis 2000M/ME	Less than 0.5 %
Conductivity	Radiometer MeterLab CDM 230	1 %

120

121 Density measurements were conducted using a vibrating-tube densimeter DMA 5000 M (Anton
 122 Paar) in the temperature range from 293.15 to 333.15 K. The apparatus was calibrated using the
 123 extended calibration procedure with dry air and degassed ultra-pure water (Elga, Veolia) with
 124 an electrolytic conductivity equals 0.055 μ S cm⁻¹ at 298.15 K. With regard to the viscosity-
 125 related errors, an automatic correction was done using the instrument by measuring the damping
 126 effect of the sample followed by a mathematical correction of the density. These measurements
 127 were performed with an uncertainty of less than ± 0.05 kg m⁻³, whereas repeatability is estimated
 128 to be ± 0.005 kg m⁻³. Temperature was measured with an uncertainty of ± 0.02 K and a resolution
 129 of ± 0.001 K.

130 The kinematic viscosity, ν , of the investigated systems was determined with a calibrated and
 131 thermostated rolling-ball viscometer (Lovis 2000 M, Anton Paar), which measures the rolling
 132 time of a ball through transparent and opaque liquids according to Hoppeler's falling-ball
 133 principle. The microviscometer is equipped with three calibrated glass capillaries of different
 134 diameter (1.59, 1.8 and 2.5) mm and steel balls. The dynamic viscosity, η , is obtained by
 135 measuring the time taken by the steel ball to fall from one side to the end of the capillary filled
 136 with the sample at a certain angle and temperature, and by knowing the density of the sample.
 137 The calibration of the capillaries was done using viscosity standards provided by the
 138 manufacturer and with water. The viscosity was measured with accuracy better than $\pm 0.5\%$
 139 (with the same ball and depending on the size of the capillary and the temperature). The
 140 viscosities were conducted in the temperature range from 293.15 to 333.15 K, and the accuracy
 141 of the temperature measurements was ± 0.02 K.

142 The ionic conductivity, s , was measured using a CDM 230 Conductivity Meter from
 143 MeterLabTM, Radiometer analytical operating at five different frequencies (94 Hz, 375Hz,
 144 2.93kHz, 23.4kHz and 46.9kHz, depending of the conductance range) with an estimated
 145 uncertainty of 1%. The conductivity cell was a Radiometer Analytical CDC741T-6 with
 146 temperature sensor (2-pole Pt sensor, $K=1.0$ cm⁻¹, glass body). Temperature and data

147 acquisitions were made by a personal computer connected to the conductivity meter. The
148 experimental cell was calibrated with standard 0,1 mol.L⁻¹ KCl solution, and the resulting cell
149 constant was 1.0358 cm⁻¹. The temperature of the samples was controlled using cryostat
150 polystat with thermal stability \pm 0.03 K. The sample was allowed to spend about 20 min at
151 constant temperature before performing any single measurement, while 40 min at the phase
152 transition.

153 All the electrochemical measurements were performed with a three-electrode cell using a
154 GAMRY REF600 potentiostat. A home-made gold microelectrode of 200 μ m in diameter was
155 used as working electrode and a platinum grid of 1x1 cm² was used as counter electrode. The
156 reference electrode was based on the Ag⁺ / Ag electrode in a double junction compartment. It
157 consists of a silver wire immersed in a first junction containing a saturated solution of silver
158 nitrate (AgNO₃) in DES, with a sintered glass at the bottom. A second junction containing pure
159 DES was used to prevent the working solution in the main electrochemical compartment from
160 any contamination of ions (Ag⁺ and NO₃⁻) coming from the first junction containing the
161 reference electrode. Before each experiment, the working electrode was carefully cleaned by
162 mechanical grinding with a SiC paper (P4000) followed by an electrochemical cycling in a 0.1
163 mol L⁻¹ sulfuric acid aqueous solution by sweeping the potential between -1 and 1.3 V/SCE at
164 100 mV.s⁻¹ for 10 min.

165 All the electrochemical experiments were performed under a dry argon atmosphere to avoid the
166 presence of oxygen and air humidity. All experiments were performed three times.

167

168 **3. Results and discussions**

169 *3.1 Physicochemical properties*

170 Variations of the density, viscosity and conductivity of the menthol-based DES and ethaline
171 were plotted as a function of temperature (in the range 293K - 333K) at atmospheric pressure
172 on Fig. 3. The temperature dependence of these properties was gathered in Table 2 for menthol-
173 based DES. As shown on Fig. 3, the density, viscosity and conductivity values of ethaline are
174 close to some of those reported in the literature [16-21]. For a better comparison, the values
175 (from this study and from the literature) of the physicochemical parameters of ethaline have
176 been presented in Table S1. As previously mentioned by some previous work [18, 22], a
177 disparity in the thermophysical properties of DES exists by comparing the different values even
178 from a same group of researchers. This discrepancy can be due to the operating conditions or
179 the water content into the mixtures.

180

181 **Table 2.** Values of some physicochemical parameters of EMIMTFSI at different temperatures at
 182 pressure ($p= 0.1$ MPa)

T (K)	density (ρ in g.cm ⁻³)	viscosity (η in mPa.s)	conductivity (σ in mS.cm ⁻¹)
293.15	1.049065	211.70	0.545
298.15	1.045406	145.82	0.688
303.15	1.041785	103.64	0.854
308.15	1.038154	75.93	1.023
313.15	1.034511	57.13	1.215
318.15	1.030862	43.83	1.430
323.15	1.027218	34.41	1.657
328.15	1.023572	27.56	1.885
333.15	1.019928	22.44	2.180

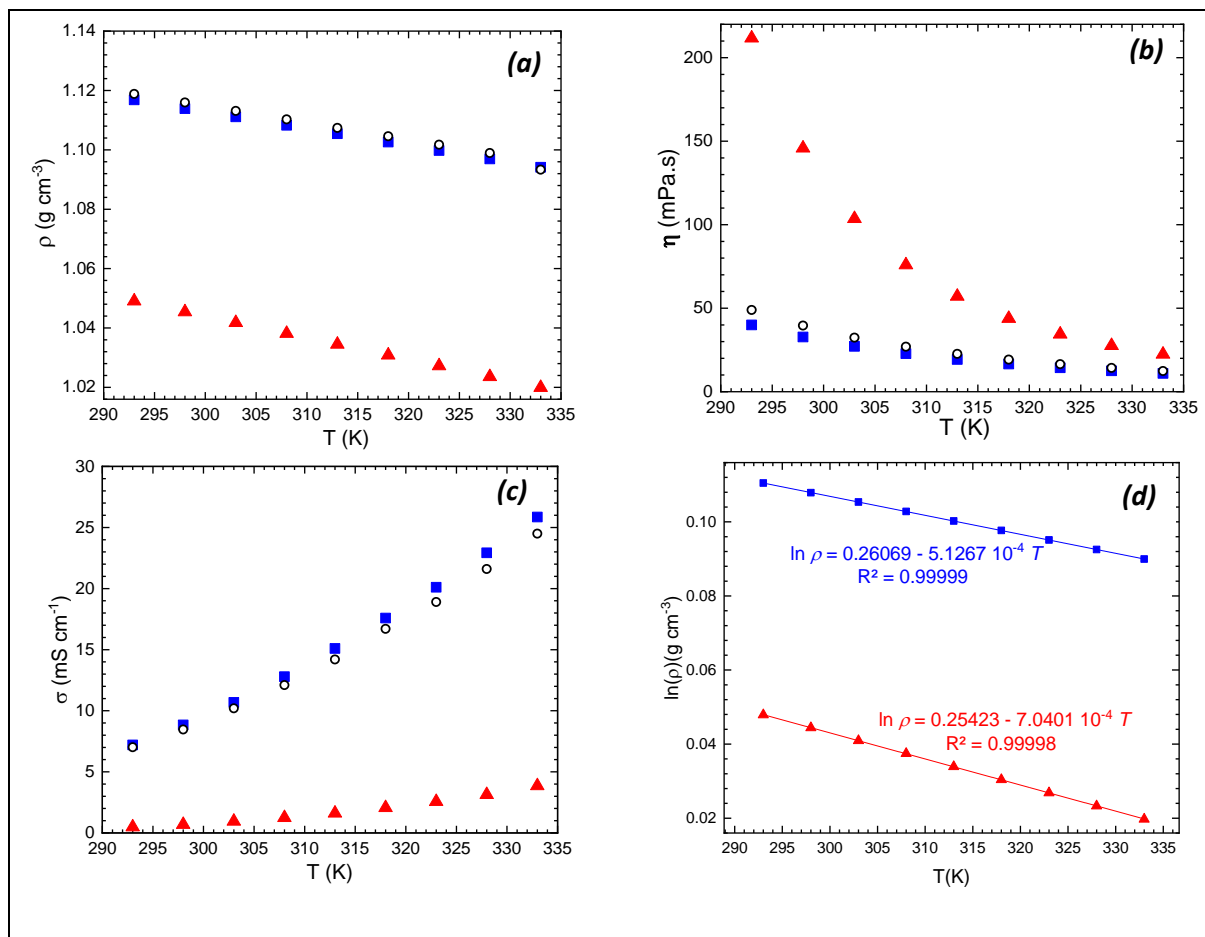
183

184 The density of both DESs decreases linearly when the temperature increases (Fig3.a), due to
 185 the molar volume increase leading to a decrease in the average distance between the molecules
 186 [23]. From the density measurements, the thermal-expansion coefficient, α , can be calculated
 187 according to

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (1)$$

188 Where V is the molar volume of the DES and T , the temperature. This thermal expansion
 189 coefficient is related to the change in volume of the medium with the temperature as shown in
 190 Eq. 1, and can be linked to the free volume in the solvent. The higher the thermal expansion
 191 coefficient, the higher the free volume. To determine these thermal expansion coefficients, the
 192 logarithm of the density ($\ln \rho$) was plotted against the temperature. A straight-line was obtained
 193 for the both DESs as shown on Fig. 3d. The slope corresponds to the thermal expansion
 194 coefficient. Table 3 gives the coefficients of thermal expansion of both DESs which were
 195 compared to the values of a common hydrophobic IL (EMIMTFSI) [24]. Similarly to
 196 imidazolium based ionic liquids, both DESs are less compressible than common organic
 197 solvents [25, 26] as toluene ($11.29 \cdot 10^{-4} \text{ K}^{-1}$ at 298.15K), dichloromethane ($13.5 \cdot 10^{-4} \text{ K}^{-1}$ at
 198 298.15K) or ethanol ($10.9 \cdot 10^{-4} \text{ K}^{-1}$ at 298.15K).

199 It can also be noticed that the thermal expansion coefficient value of the ternary mixture based
 200 on menthol is lower than the one for the binary menthol – acetic acid studied by Ribiero et al.
 201 [14] ($7 \cdot 10^{-4} \text{ K}^{-1}$ for this work compared to $9.1 \cdot 10^{-4} \text{ K}^{-1}$ for the binary mixture). The addition of
 202 ethanolamine to the menthol based-DES decreases the free volume thus leading to a less
 203 compressible solvent.



204 **Figure 3.** Variations of (a) the density, (b) the viscosity, (c) the conductivity and (d) the logarithm of
 205 the density as a function of the temperature of the DESs - ethaline (blue squares); ethaline from ref.
 206 [18] (black circles); and DES-Menthol (red triangles).

207
 208 The dynamic viscosity, η , defines the internal resistance of a fluid to a shear stress. The
 209 knowledge of its value is of interest for electrochemical applications due to its strong effect on
 210 the mass transport properties in the solution that significantly affects the diffusion of
 211 electroactive species in the media. The variations of the DES viscosity as a function of the
 212 temperature are reported in Fig. 3b. This viscosity profile is similar to what is usually observed
 213 in the literature for DES mixtures [7, 27, 28], with a more or less marked exponential decrease
 214 of the viscosity with the increase of the temperature. In a DES, the viscosity is mainly related
 215 to the formation of hydrogen bonds and van der Waals interactions. Menthol-based DES

216 exhibits higher viscosity than ethaline. For example, at 298 K, the viscosity of menthol-based
 217 DES is 145 mPa.s, that is, about four times larger than viscosity of ethaline (33 mPa.s) at the
 218 same temperature. Such a high viscosity for menthol-based DES may be ascribed to the
 219 presence of a strong hydrogen-bond network between all the components.

220 The temperature dependence of the viscosity values is most often fitted using an Arrhenius-like
 221 relationship, which expresses as

222

$$\ln \eta = \ln \eta^\infty + \frac{E_\eta}{RT} \quad (2)$$

223 Where E_η is the activation energy, η the viscosity, η^∞ the pre-exponential factor and R the
 224 perfect gas constant. E_η is the energy barrier that must be overcome by the ions to move through
 225 the medium. The larger E_η , the harder for the ions to move in the liquid. This equation is based
 226 on the empirical relationship of Arrhenius for the temperature dependence of reaction rates.
 227 Most of the time, Eq.2 can be applied to describe the temperature dependence of the viscosity
 228 in a narrow temperature range. For larger temperature range, another empirical approach the
 229 so-called Vogel-Tamman-Fulcher (VTF) relationship is commonly used to describe this
 230 temperature dependence [29]. In parallel, in order to give a better understanding of the viscous
 231 flow with a thermodynamic light, many authors rely on the Eyring's transition state theory
 232 applied to the viscosity [30]. In this approach, the viscosity of a liquid is given by

$$\eta = \frac{h\mathcal{N}_a}{V} \exp\left(\frac{\Delta G^\ddagger}{RT}\right) \quad (3)$$

233 where ΔG^\ddagger is the molar Gibbs free energy of activation of the viscous flow, h the Planck's
 234 constant, \mathcal{N}_a the Avogadro's number and V the molar volume of the liquid, which can be
 235 expressed as,

$$V = \frac{M}{\rho} \quad (4)$$

236 with ρ the density of the considered DES and M its molar mass.

237 From Eq. 3 the following expanded relation is obtained

$$\ln \eta = \ln\left(\frac{h\rho\mathcal{N}_a}{M}\right) - \frac{\Delta S^\ddagger}{R} + \frac{\Delta H^\ddagger}{RT} \quad (5)$$

238

239 Where ΔH^\ddagger and ΔS^\ddagger are the enthalpy and entropy of activation, respectively. By comparison
 240 of Eq. 2 and Eq. 5, it comes

$$\eta^\infty = \frac{h\rho N_a}{M} \exp\left(-\frac{\Delta S^\ddagger}{R}\right) \quad (6)$$

241 and

$$E_\eta \approx \Delta H^\ddagger \quad (7)$$

242 Eq. 6 shows why some authors introduce the pre-exponential factor of the Arrhenius-like
 243 relation as an entropic term. This also shows that Eq. 2 can be modelled by a straight-line only
 244 for narrow temperature range, which widely depends on the variation of the density with the
 245 temperature. Thus, $E_\eta = \Delta H^\ddagger$ only if the density can be considered as constant in the
 246 investigated temperature range. Nevertheless, by plotting $\ln\left(\frac{M\eta}{h\rho N_a}\right)$ as a function of T^{-1} for the
 247 studied DES, ΔH^\ddagger and ΔS^\ddagger were determined and presented in Table 3, with the value of E_η
 248 determined from Eq. 2. As expected, the activation energy is very close to the enthalpy of
 249 activation. Moreover, the values of activation entropy are of interest. As shown in Table 3,
 250 DES-menthol has the highest activation entropy when compared to both ethaline and
 251 EMIMTFSI: indeed, DES-menthol contains the larger number of compounds.

252

253 **Table 3.** Characteristic parameters for density, viscosity and conductivity variations of the DESs and
 254 EMIMTFSI determined from their variations as a function of the temperature

Medium	M (/g mol ⁻¹)	α (/10 ⁻⁴ K ⁻¹)	E_η (/kJ mol ⁻¹)	E_σ (/kJ mol ⁻¹)	ΔH^\ddagger (/kJ mol ⁻¹)	ΔS^\ddagger (/J K ⁻¹ mol ⁻¹)
Ethaline	87.7	5.1	26.2	25.9	25.8	13.6
DES-Menthol	74.1	7.0	45.4	41.6	44.8	66.0
EMIMTFSI*	391.3	6.6	23.4	20.8	22.8	-5.5

255 *from ref [24]

256

257 Fig. 3c shows that the conductivity of both DESs increases almost linearly with the temperature.
 258 This is a direct consequence of a faster movement of ions in the media at higher temperatures.
 259 At room temperature, the conductivity of ethaline is about 8.8 mS.cm⁻¹, which is more than one
 260 order of magnitude higher than the conductivity measured for the menthol-based DES (0.7
 261 mS.cm⁻¹). Such a difference may be ascribed, at least partially, to the higher viscosity of the

262 menthol-based DES. The conductivity of an ion, σ_i , is linked to its diffusion coefficient, D_i , as
 263 expressed by the Nernst-Einstein equation,

$$\sigma_i = \frac{c_i z_i^2 \mathcal{F}^2 D_i}{RT} \quad (8)$$

264 where c_i stands for the concentration of the ion i and z_i its charge. Usually, the diffusion
 265 coefficient is linked to the viscosity by the Stokes-Einstein relation, defined for a model
 266 spherical species i of an effective radius r_i , as

$$D_i = \frac{k_B T}{6\pi r_i \eta} \quad (9)$$

267 This relation is commonly used to determine the diffusion coefficient of species in IL. However,
 268 this latter equation is only valid if the ion i is bigger than the species constituting the medium,
 269 but there are other relations linking the diffusion coefficient to the reverse of the viscosity taking
 270 into account, for example, the different characteristic lengths between the species [31].
 271 Anyhow, we have to keep in mind that the diffusion coefficient is inversely proportional to the
 272 viscosity. By taking account Eqs. 8 and 9, the conductivity of an ion can be expressed as

$$\sigma_i = \frac{c_i z_i^2 \mathcal{F}^2}{6\pi \mathcal{N}_a r_i \eta} \quad (10)$$

273 The conductivity of the mixtures is the sum of ionic conductivities of the anion and the cation.

$$\sigma = \sigma_{anion} + \sigma_{cation} = \frac{\mathcal{F}^2}{6\pi \mathcal{N}_a \eta} \left(\frac{c_{anion} z_{anion}^2}{r_{anion}} + \frac{c_{cation} z_{cation}^2}{r_{cation}} \right) \quad (11)$$

274 In our case, $c_{anion} = c_{cation} = c_{salt}$, then

$$\sigma = \frac{\mathcal{F}^2}{6\pi \mathcal{N}_a \eta} \frac{x_{salt}}{M} \rho \left(\frac{1}{r_{anion}} + \frac{1}{r_{cation}} \right) \quad (12)$$

275 x_{salt} is the molar fraction of the salt in the mixture, ($x_{salt} = 1$, for neat IL). Combining Eq. 12 with
 276 Eq. 2, an Arrhenius-like relationship is obtained

$$\ln \sigma = \ln \sigma^\infty - \frac{E_\sigma}{RT} \quad (13)$$

277 Where σ^∞ is a constant and E_σ is the activation energy for ionic conductivity. E_σ of the DESs
 278 and EMIMTFSI determined from the experimental data using Eq. 13 are shown in Table 2.

279 By considering, Eqs. 5 and 13, the following expression is then obtained

$$\ln \sigma = \ln \left(\frac{F^2 x_{salt}}{6\pi N_a^2 h} \left(\frac{1}{r_{anion}} + \frac{1}{r_{cation}} \right) \right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (14)$$

280

281 Knowing the activation entropy and enthalpy, only the sum $\left(\frac{1}{r_{anion}} + \frac{1}{r_{cation}} \right)$ can be calculated.

282 As shown in table 3, this value decreases as the temperature increases.

283

284 **Table 3.** Variation of the sum $\left(\frac{1}{r_{anion}} + \frac{1}{r_{cation}} \right)$ as a function of the temperature

Temperature (/K)	ethaline $\sum_i \frac{1}{r_i}$ (/m)	DES-Menthol $\sum_i \frac{1}{r_i}$ (/m)	EMIMTFSI* $\sum_i \frac{1}{r_i}$ (/m)
293	9.07 10 ⁹	3.23 10 ⁹	5.32 10 ⁹
298	8.30 10 ⁹	3.00 10 ⁹	5.44 10 ⁹
303	7.61 10 ⁹	2.76 10 ⁹	5.49 10 ⁹
308	7.02 10 ⁹	2.48 10 ⁹	5.44 10 ⁹
313	6.47 10 ⁹	2.23 10 ⁹	5.35 10 ⁹
318	5.96 10 ⁹	2.00 10 ⁹	5.23 10 ⁹
323	5.44 10 ⁹	1.78 10 ⁹	5.09 10 ⁹
328	5.01 10 ⁹	1.57 10 ⁹	4.96 10 ⁹
333	4.60 10 ⁹	1.42 10 ⁹	4.93 10 ⁹

285

*from ref [24]

286

287 For these three media the ions are different as well as their environment. At this stage, the
 288 analysis of these data is difficult. Indeed, first, it is necessary to check that the hypothesis of
 289 Stokes-Einstein concerning the size of the ions is always valid. Afterwards, we need an
 290 assumption or other analysis or calculation to differentiate the anion from the cation. For
 291 EMIMTFSI, the cation radius can be evaluated by taking the anion radius available in the
 292 literature [32, 33], $r_{TFSI} = 3.65 \text{ \AA}$. Thus, at 298K, the radius of the cation EMIM is around 3.7
 293 \AA . For DES, to our knowledge, there is no value for ionic radius, since the environment is very
 294 different, we chose to only calculate an average radius at 298K to compare these two different
 295 mixtures. At 298 K, the average radius is about 2.4 \AA in ethaline and 6.7 \AA in menthol-based
 296 DES.

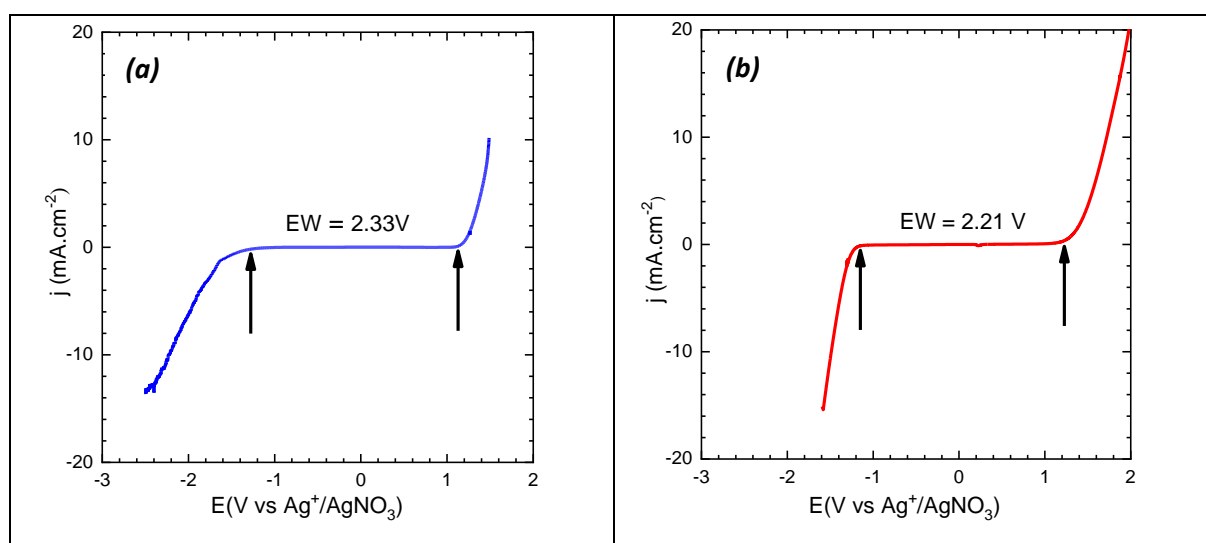
297

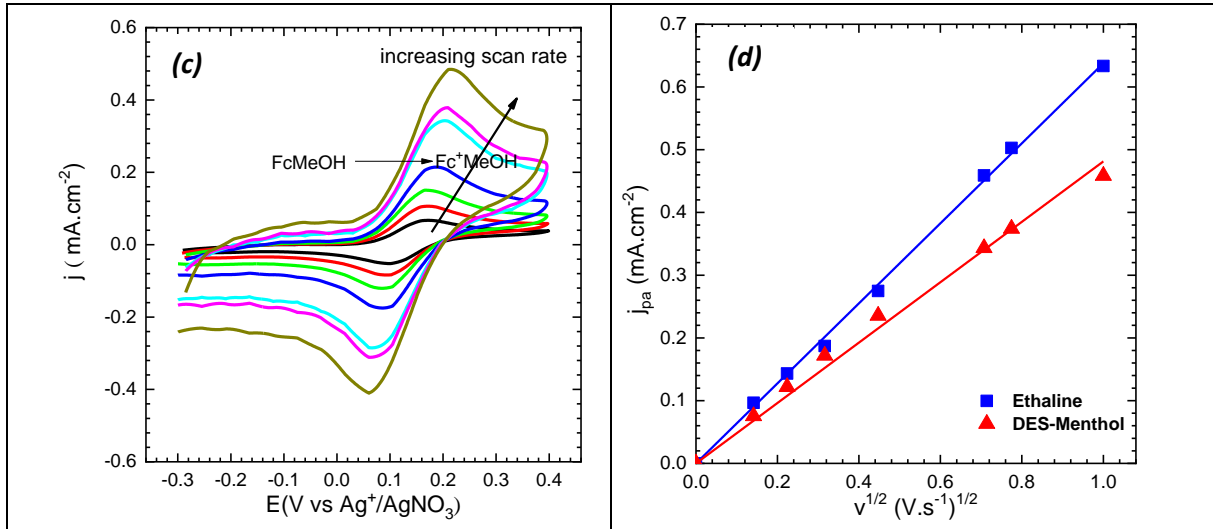
298 3.2 Electrochemical properties

299 Before envisioning any practical electrochemical application, it is of interest to determine the
300 electrochemical window (EW) of the solvents. Figs. 4a and b show the EW of each DES
301 measured using linear sweep voltammetry (LSV) from -2.5 to 2 V/ $\text{Ag}^+/\text{AgNO}_3$ using a 200 μm
302 in diameter gold electrode. Unlike aprotic ionic liquids, which usually have broad
303 electrochemical windows spreading over 4 to 5 V [34], the DESs studied in this work display a
304 lower electrochemical stability comprised in the range 2 to 2.5 V (taking a cutoff value for the
305 current density of $\pm 100 \mu\text{A cm}^{-2}$). However, this EW is twice larger than the EW of water
306 electrolyte, which makes these DESs attractive for electrochemical applications.

307 The electrochemical behavior of an electroactive species, the hydroxymethylferrocene
308 (FcMeOH), in DES_s was then studied by cyclic voltammetry (CV) by varying the scan rates
309 (Fig. 4c). CVs clearly exhibit a quasi-reversible behavior, in which the ratio between the current
310 density of the anodic peak j_{pa} and that of the cathodic peak j_{pc} is close to 1 also at low scan rates
311 whereas the difference between the anodic and cathodic peak potentials is in agreement with
312 the predicted values ($E_{pa} - E_{pc} \approx 60 \text{ mV}$) for a mass-transfer controlled system [35]. The current
313 density peak (j_{p1}) varies linearly with the square root of the scan rate (Fig. 4d) showing that the
314 mass transfer of FcMeOH in the investigated DESs is controlled by the diffusion of
315 electroactive species [35].

316





317 **Figure 4.** LSV of (a) ethaline and (b) DES-Menthol at a scan rate of 5mVs^{-1} ; (c) CV of a 5mM
 318 FcMeOH in menthol-based DES at different scan rates (from 20 to 1000mVs^{-1}); (d) variation of the
 319 current density peak j_{pa} with the square root of the scan rate for the FcMeOH oxidation in DES. All
 320 these experiments were performed, at $(25 \pm 0.1)^\circ\text{C}$, with a gold working electrode ($200 \mu\text{m}$ in
 321 diameter).

322

323 On this scan rate domain, the diffusion coefficient of FcMeOH can thus be obtained from the
 324 slope of the current intensity curve as a function of square root of sweep rate by using Randles-
 325 Sevcik equation

$$i_p = 0.446nF \sqrt{\frac{nFv}{RT}} C_i A \sqrt{D_i} \quad (15)$$

326 where i_p is the current of the peak, n the number of electron exchanged, A the electrode surface
 327 area, F the Faraday constant, D_i the diffusion coefficient, C_i the concentration of the
 328 electroactive species i , and v the scan rate.

329

330 **Table 4** Variation of the diffusion coefficient of ferrocene methanol as a function of the viscosity of the
 331 medium

Medium @298K	η (/mPa.s)	D (/ $10^{-7}\text{cm}^2.\text{s}^{-1}$)
EMIMTFSI*	30.4	3.5
Ethaline	32.7	2.2
DES-Menthol	146	1.1

335

336

*from ref [24]

337 The diffusion coefficients values of FcMeOH in DESs are presented in Table 3. It should be
338 noticed that the diffusion coefficients obtained in DESs are of the same order of magnitude than
339 those obtained in the pure ionic liquid (*e.g.* EMIMTFSI). In ethaline the diffusion coefficient
340 of FcMeOH is twice than in the menthol-based DES. Indeed, as shown in Table 4, ethaline has
341 a lower viscosity, which explains the more efficient mass transport corresponding to higher
342 value of the diffusion coefficient. Interestingly, the diffusion coefficient of FcMeOH is of the
343 same order of magnitude in the DESs and IL studied in this work, showing the great potentials
344 of the new menthol-based DESs.

345

346 **4. Conclusions**

347 Two deep eutectic solvents (DESs), ethaline and menthol-based DES, have been prepared and
348 characterized. Hydrophobicity test was performed to show the role of menthol in the mixture.
349 The addition of ethanolamine to the menthol – acetic acid mixture leads to an increase of the
350 conductivity. Their physicochemical properties including density, viscosity and conductivity
351 were studied in detail at different temperatures. Although these mixtures are no conventional,
352 we estimated an average radius of the ions assuming that the Stokes-Einstein relationship can
353 be applied.

354 LSV curves at low scan rate allowed obtaining the electrochemical window of DESs. The
355 electrochemical windows of the two DESs do not show significant differences and are about
356 2.4 V. The redox couple FcMeOH⁺/FcMeOH is reversible in menthol-based DES and the
357 diffusion coefficient of FcMeOH is of the same order of magnitude as that obtained in the pure
358 ionic liquid (EMIMTFSI), thus showing than this DES is suited for performing electrochemical
359 experiments.

360 Menthol-based DESs are thus a good alternative to hydrophobic ionic liquid for electrochemical
361 applications (*e.g.* for battery application) especially since it is a biocompatible solvent, easy to
362 synthesize and cheap.

363

364

365 **Acknowledgements**

366 This work was supported by the Ecole Doctorale Chimie Physique et Chimie Analytique de
367 Paris Centre (ED 388).

368

369 **References**

- 370 [1] M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, Ionic-liquid materials for the
371 electrochemical challenges of the future, *Nat Mater* 8 (2009) 621-629.
- 372 [2] V.L. Martins, R.M. Torresi, Ionic liquids in electrochemical energy storage, *Curr. Opin. Electrochem.*
373 9 (2018) 26-32.
- 374 [3] Y. Hu, Z. Wang, X. Huang, L. Chen, Physical and electrochemical properties of new binary room-
375 temperature molten salt electrolyte based on LiBETI and acetamide, *Solid State Ionics* 175 (2004) 277-
376 280.
- 377 [4] S.B. Capelo, T. Mendez-Morales, J. Carrete, E. Lopez Lago, J. Vila, O. Cabeza, J.R. Rodriguez, M.
378 Turmine, L.M. Varela, Effect of temperature and cationic chain length on the physical properties of
379 ammonium nitrate-based protic ionic liquids, *J. Phys. Chem. B* 116 (2012) 11302-11312.
- 380 [5] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep eutectic solvents (DESs) and their applications, *Chem. Rev.*
381 114 (2014) 11060-11082.
- 382 [6] C.J. Clarke, W.C. Tu, O. Levers, A. Brohl, J.P. Hallett, Green and Sustainable Solvents in Chemical
383 Processes, *Chem. Rev.* 118 (2018) 747-800.
- 384 [7] M.A. Kareem, F.S. Mjalli, M.A. Hashim, I.M. AlNashef, Phosphonium-Based Ionic Liquids Analogues
385 and Their Physical Properties, *J. Chem. Eng. Data* 55 (2010) 4632-4637.
- 386 [8] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of
387 choline chloride/urea mixtures, *Chem Commun (Camb)* (2003) 70-71.
- 388 [9] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Deep eutectic solvents formed
389 between choline chloride and carboxylic acids: Versatile alternatives to ionic liquids, *J. Am. Chem. Soc.*
390 126 (2004) 9142-9147.
- 391 [10] C. Teja, F.R. Nawaz Khan, Choline Chloride-Based Deep Eutectic Systems in Sequential Friedlander
392 Reaction and Palladium-Catalyzed sp(3) CH Functionalization of Methyl Ketones, *ACS Omega* 4 (2019)
393 8046-8055.
- 394 [11] A. Yadav, S. Pandey, Densities and Viscosities of (Choline Chloride + Urea) Deep Eutectic Solvent
395 and Its Aqueous Mixtures in the Temperature Range 293.15 K to 363.15 K, *J. Chem. Eng. Data* 59 (2014)
396 2221-2229.
- 397 [12] Q.H. Zhang, K.D. Vigier, S. Royer, F. Jerome, Deep eutectic solvents: syntheses, properties and
398 applications, *Chemical Society Reviews* 41 (2012) 7108-7146.
- 399 [13] C. Florindo, L.C. Branco, I.M. Marrucho, Development of hydrophobic deep eutectic solvents for
400 extraction of pesticides from aqueous environments, *Fluid Phase Equilib.* 448 (2017) 135-142.
- 401 [14] B.D. Ribeiro, C. Florindo, L.C. Iff, M.A.Z. Coelho, I.M. Marrucho, Menthol-based Eutectic Mixtures:
402 Hydrophobic Low Viscosity Solvents, *ACS Sustainable Chemistry & Engineering* 3 (2015) 2469-2477.
- 403 [15] P. Bonhote, A.P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, Hydrophobic,
404 highly conductive ambient-temperature molten salts (vol 35, pg 1168, 1996), *Inorg. Chem.* 37 (1996)
405 166-166.
- 406 [16] A. Yadav, J.R. Kar, M. Verma, S. Naqvi, S. Pandey, Densities of aqueous mixtures of (choline
407 chloride+ethylene glycol) and (choline chloride+malonic acid) deep eutectic solvents in temperature
408 range 283.15–363.15K, *Thermochim. Acta* 600 (2015) 95-101.
- 409 [17] A.R. Harifi-Mood, R. Buchner, Density, viscosity, and conductivity of choline chloride + ethylene
410 glycol as a deep eutectic solvent and its binary mixtures with dimethyl sulfoxide, *J. Mol. Liq.* 225 (2017)
411 689-695.
- 412 [18] D. Lapeña, L. Lomba, M. Artal, C. Lafuente, B. Giner, Thermophysical characterization of the deep
413 eutectic solvent choline chloride:ethylene glycol and one of its mixtures with water, *Fluid Phase Equilib.*
414 492 (2019) 1-9.
- 415 [19] F.S. Mjalli, O.U. Ahmed, Ethaline and Glyceline binary eutectic mixtures: characteristics and
416 intermolecular interactions, *Asia-Pac. J. Chem. Eng.* 12 (2017) 313-320.
- 417 [20] H. Shekaari, M.T. Zafarani-Moattar, M. Mokhtarpour, S. Faraji, Volumetric and compressibility
418 properties for aqueous solutions of choline chloride based deep eutectic solvents and Prigogine–Flory–

419 Patterson theory to correlate of excess molar volumes at $T = (293.15 \text{ to } 308.15) \text{ K}$, *J. Mol. Liq.* 289
420 (2019).

421 [21] H. Shekaari, M. Taghi Zafarani-Moattar, M. Mokhtarpour, S. Faraji, Compatibility of sustainable
422 solvents ionic liquid, 1-ethyl-3-methylimidazolium ethyl sulfate in some choline chloride based deep
423 eutectic solvents: thermodynamics study, *J. Chem. Thermodyn.* 141 (2020) 105961.

424 [22] H. Shekaari, M.T. Zafarani-Moattar, M. Mokhtarpour, S. Faraji, Volumetric and compressibility
425 properties for aqueous solutions of choline chloride based deep eutectic solvents and Prigogine–Flory–
426 Patterson theory to correlate of excess molar volumes at $T = (293.15 \text{ to } 308.15) \text{ K}$, *J. Mol. Liq.* 289
427 (2019) 111077.

428 [23] F. Chemat, H. Anjum, A.M. Shariff, P. Kumar, T. Murugesan, Thermal and physical properties of
429 (Choline chloride + urea + l-arginine) deep eutectic solvents, *J. Mol. Liq.* 218 (2016) 301-308.

430 [24] R. Khalil, N. Chaabene, M. Azar, I.B. Malham, M. Turmine, Effect of the chain lengthening on
431 transport properties of imidazolium-based ionic liquids, *Fluid Phase Equilib.* 503 (2020) 112316.

432 [25] Z. Gu, J.F. Brennecke, Volume Expansivities and Isothermal Compressibilities of Imidazolium and
433 Pyridinium-Based Ionic Liquids, *J. Chem. Eng. Data* 47 (2002) 339-345.

434 [26] C. Caleman, P.J. van Maaren, M. Hong, J.S. Hub, L.T. Costa, D. van der Spoel, Force Field Benchmark
435 of Organic Liquids: Density, Enthalpy of Vaporization, Heat Capacities, Surface Tension, Isothermal
436 Compressibility, Volumetric Expansion Coefficient, and Dielectric Constant, *J Chem Theory Comput* 8
437 (2012) 61-74.

438 [27] E.A. Crespo, J.M.L. Costa, A.M. Palma, B. Soares, M.C. Martín, J.J. Segovia, P.J. Carvalho, J.A.P.
439 Coutinho, Thermodynamic characterization of deep eutectic solvents at high pressures, *Fluid Phase*
440 *Equilib.* 500 (2019).

441 [28] N.F. Gajardo-Parra, M.J. Lubben, J.M. Winnert, Á. Leiva, J.F. Brennecke, R.I. Canales,
442 Physicochemical properties of choline chloride-based deep eutectic solvents and excess properties of
443 their pseudo-binary mixtures with 1-butanol, *J. Chem. Thermodyn.* 133 (2019) 272-284.

444 [29] N.S.M. Vieira, I. Vázquez-Fernández, J.M.M. Araújo, N.V. Plechkova, K.R. Seddon, L.P.N. Rebelo,
445 A.B. Pereiro, Physicochemical Characterization of Ionic Liquid Binary Mixtures Containing 1-Butyl-3-
446 methylimidazolium as the Common Cation, *J. Chem. Eng. Data* 64 (2019) 4891-4903.

447 [30] J.F. Kincaid, H. Eyring, A.E. Stearn, The Theory of Absolute Reaction Rates and its Application to
448 Viscosity and Diffusion in the Liquid State, *Chem. Rev.* 28 (1941) 301-365.

449 [31] H. Eyring, Viscosity, plasticity, and diffusion as examples of absolute reaction rates, *J. Chem. Phys.*
450 4 (1936) 283-291.

451 [32] G.B. Appetecchi, M. Montanino, D. Zane, M. Carewska, F. Alessandrini, S. Passerini, Effect of the
452 alkyl group on the synthesis and the electrochemical properties of N-alkyl-N-methyl-pyrrolidinium
453 bis(trifluoromethanesulfonyl)imide ionic liquids, *Electrochim. Acta* 54 (2009) 1325-1332.

454 [33] H. Shirota, A.M. Funston, J.F. Wishart, E.W. Castner, Jr., Ultrafast dynamics of pyrrolidinium cation
455 ionic liquids, *J. Chem. Phys.* 122 (2005) 184512.

456 [34] M. Galiński, A. Lewandowski, I. Stępnia, Ionic liquids as electrolytes, *Electrochim. Acta* 51 (2006)
457 5567-5580.

458 [35] A.J. Bard, L.R. Faulkner, J. Leddy, C.G. Zoski, *Electrochemical methods: fundamentals and*
459 *applications*. Wiley New York, 1980.

460