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Green monoterpenes based deep eutectic solvents for effective BTEX absorption from biogas

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15 **ABSTRACT:**

16 The combustion of biogas which contains significant amounts of monoaromatic
17 hydrocarbons, i.e. benzene, ethylbenzene, toluene, and xylene (BTEX) can cause many
18 technological, environmental, and health problems. Therefore, in these studies, a new physical
19 absorption method based on deep eutectic solvents (DES) consisting of monoterpenes and
20 carboxylic acids was developed for BTEX removal. A total of 39 DES were synthesized, of
21 which seven were selected based on their affinity to BTEX, favorable physicochemical
22 properties, and “green” character. Detailed structural (i.e. ¹H NMR, ¹³C NMR, and FT-IR)
23 and physicochemical experiments (i.e. melting point, density, viscosity, and surface tension)
24 were performed for the DES. Then, DESs were used for the absorption process in both the
25 laboratory and enlarged scale. BTEX absorption was monitored using two methods, including
26 "in-situ" gas chromatography, and "online" sensors matrices. The crucial absorption

27 parameters i.e. type of DES, temperature, and regeneration possibility were carefully studied.
28 The mechanism of BTEX absorption was explained using experimental spectroscopic
29 techniques and theoretical analysis based on the COSMO-RS model. The obtained results
30 indicate that Eucalyptol:Octanoic acid can selectively capture BTEX from a biogas mixture
31 due to the formation of electrostatic interaction. DES absorption capacity is 53.96 mg/g,
32 which is comparable with commercially available absorbents.

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34 **KEYWORDS:** monoterpenes, monoaromatic hydrocarbons, BTEX, biogas, absorption,
35 deep eutectic solvents

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39 **1. INTRODUCTION**

40 Currently, an increase in demand for renewable energy production from natural sources
41 can be observed. This is due to a number of factors, including the introduction of increasingly
42 stringent climate policies limiting coal mining or assuming a phase-out of nuclear power
43 plants, as well as the current war-induced fuel crisis. Therefore, more and more countries are
44 considering the use of biogas from waste materials as renewable energy that could make
45 countries less dependent on energy imports. The main problem in the widespread use of
46 biogas is the presence of large amounts of organic and inorganic pollutants. Till now, many
47 methods have been developed to purify biogas from inorganic substances, but there are still
48 few technologies dedicated to the removal of volatile organic compounds from the biogas
49 stream. One of the groups of problematic substances in biogas is monoaromatic
50 hydrocarbons including benzene, toluene, ethylbenzene, and xylenes (BTEX). These
51 compounds are also one of the most common chemical pollutants of air, natural, and waste



52 gasses [1,2]. The presence of BTEX in biogas streams is mainly caused by the volatilization
53 of intermediate products formed during fermentation processes. The concentration of BTEX
54 in biogas streams can vary significantly depending on the raw material used in the
55 fermentation process. Nevertheless, the concentration may vary from 94 to 1906 mg/m³ [3].
56 The presence of BTEX in biogas streams is unfavorable from ecological, public health, and
57 industrial point of view [4,5]. Most of BTEX have a confirmed carcinogenic potential and
58 adverse effects on the water and air environment [6–8]. In addition, combustion of biogas
59 containing high concentrations of BTEX can cause corrosion, contamination, and clogging of
60 engine systems [9,10]. Therefore, it is essential to remove monoaromatic hydrocarbons from
61 biogas streams.

62 Currently, in the literature, we can find several methods dedicated to the removal of
63 BTEX from biogas, including: absorption, catalytic oxidation, conventional adsorption,
64 pressure swing adsorption, thermal swing adsorption, membrane, biological, and cryogenic
65 methods [11–16]. Nevertheless, some of these methods show only low BTEX removal
66 efficiency, long-time operation, require the use of toxic organic solvents, high capital
67 investment, and running costs [17]. Therefore, the development of a cost-effective, efficient,
68 "green" technology for BTEX removal from biogas streams is a major challenge for the
69 energy industry. One of the most widely used industrial technology for volatile organic
70 compounds (VOCs) captured from biogas is physical absorption. Physical scrubbing has some
71 pros, including low operation and investment cost, good efficiency, and can be considered
72 environmentally friendly if appropriate absorbents are used [18]. Among the available
73 absorbents, the following can be distinguished triethylene glycol [19], fluorocarbon
74 surfactants [20], polyethylene glycol, paraffin, water emulsion [21], and amines [22].
75 However, most of these solvents are toxic and difficult to separate from the volatile organic
76 compounds for the recycling process [23]. The green absorbent materials should be



77 characterized by low vapor pressure, high boiling point, low viscosity, high absorption
78 capacity, low cost and should be easy to regenerate [24].

79 Until recently, ionic liquids have been considered the ideal absorbents for the capture of
80 BTEX from gaseous fuel streams [23]. However, their high price, non-biodegradable, and
81 frequently toxic properties make them not widely used in the industrial purification of gaseous
82 streams. In order to overcome the disadvantages of ionic liquids, a new type of green solvents
83 named deep eutectic solvents (DESs) started to be considered as efficient media for biogas
84 purification. According to the definition, DES is a complex which is consisting of a hydrogen
85 bond donor (HBD) and hydrogen bond acceptor (HBA) with appropriate molar ratios. The
86 specific non-covalent interactions created between HBA and HBD lead to the formation of
87 DES with a much lower melting point compared to the individual components [25,26]. So far,
88 many new DESs have been synthesized and successfully used in many separation processes,
89 such as extraction, microextraction, absorption, and adsorption [27–32]. Literature data show
90 that DES is characterized by a high absorption capacity of carbon dioxide and other inorganic
91 pollutants (including ammonia, hydrogen sulfide, water vapor, and sulfur dioxide) occurring
92 in gaseous fuels, i.e. biogas. However, to ensure high efficiency of the removal of individual
93 contaminants, it is necessary to choose the appropriate substances for DES formation. This is
94 a crucial parameter because, as proven in previous works, the driving force of absorption
95 processes using DES are non-covalent interactions between the absorbent and impurities, i.e.,
96 hydrogen bonds or electrostatic interactions. For example, to absorb CO₂ (hydrogen bond
97 acceptor), it is necessary to use a DES that has at least one hydrogen bond donor group in the
98 structure, i.e. -OH, -COOH, or -NH₂. The opposite is true for ammonia, which, due to its
99 structure, is a good hydrogen bond donor, therefore a suitable DES for absorption should have
100 acceptor groups, i.e. =O, or -O- [33–38]. The mechanisms for removing inorganic
101 contaminants from gas are currently fairly well known. Therefore, it is easy to speculate



102 which DES might be suitable for capturing selected substances. However, knowledge of the
103 VOC absorption capacity of gaseous streams with DES is very limited. Until now, the high
104 absorption capacity of deep eutectic solvents has been proven for volatile organic silicon
105 [24,32,39,40], sulfur [41], and chlorine compounds [42]. Among the compounds from the
106 BTEX group, an attempt has been made to remove toluene from biogas [43,44]. To the best of
107 our knowledge, there are no works dedicated to the removal of all BTEX compounds from
108 gas streams by means of deep eutectic solvents.

109 The paper describes the synthesis of new green monoterpenes based on deep eutectic
110 solvents, their structural, and physicochemical properties (i.e. density, viscosity, surface
111 tension, and melting point) as well as the application as efficient absorbents for BTEX capture
112 from biogas. In this study, structural characterization of new absorbent materials and
113 interaction between BTEX, and DES were analyzed using theoretical method based on the
114 COSMO-RS model, and experimental techniques based on proton and carbon-13 nuclear
115 magnetic resonance (^1H NMR and ^{13}C NMR), as well as Fourier transform infrared
116 spectroscopy (FTIR). The absorption process was optimized in terms of the selection of the
117 appropriate DES, and absorption temperature. Under optimal conditions, the absorption
118 efficiency of DES was compared with a commercially available absorbent dedicated to biogas
119 purification. The absorption processes were monitored using two methods, gas
120 chromatography, and sensor matrices. The comparison of the two methods of process control
121 was aimed at confirming the usefulness of the sensors' matrices in online research, due to
122 shorter time of single analysis and its lower costs. The use of sensor arrays allow a real-time
123 control of the absorption process, which in combination with an appropriately selected control
124 algorithm can make the process fully autonomous (requiring little control by personnel). The
125 validity of using gas sensor matrices as an alternative to chromatographic techniques has
126 already been demonstrated, e.g. to control biofiltration process [45–48], odour monitoring



127 [49], methane reforming process monitoring [50] and they also have high application potential
128 in food industry [51] or pharmaceutical industry [52].

129 **2. MATERIALS AND METHODS**

130

131 **2.1. Materials**

132 The following substances were used for the preparation of DES: \pm camphor (Cam),
133 carvone (C-one), eucalyptol (Eu), furfural (Fu), choline chloride (ChCl),
134 tetramethylammonium bromide (TMABr), tetraethylammonium bromide (TEABr),
135 tetrapropylammonium bromide (TPABr), tetrabutylammonium bromide (TBABr), guaiacol
136 (G), syringol (S), menthol (M), thymol (Th), vanillin (V), formic acid (FA), octanoic acid
137 (OA), nonanoic acid (NA), decanoic acid (DA), dodecanoic acid (DDA) and levulinic acid
138 (Lev). For the preparation of contaminated biogas, monoaromatic hydrocarbons including
139 benzene, toluene, ethylbenzene, and xylene were used. All reagents were obtained from
140 Sigma Aldrich (St. Louis, MO, USA) with high purity ($\geq 98\%$). For the comparison of DES
141 efficiency, a commercially available absorbent Genosorb[®] 1843 (Clariant, USA) was used.
142 High purity gases including nitrogen (purity N 5.0), methane (purity N 5.5), and carbon
143 dioxide (purity N 4.5) were obtained from Linde Gas (Poland). The air was generated by a
144 DK50 compressor with a membrane dryer (Ekkom, Poland), and hydrogen (purity N 5.5)
145 generated by Precision Hydrogen 1200 Generator (PEAK Scientific, Scotland, UK). All gases
146 were used for the preparation of a model biogas streams and chromatographic analysis.

147

148 **2.2. Procedures**

149 **2.2.1. Preparation of DESs**

150 DESs were prepared using the method described in previous studies [40–42]. Two
151 chemical compounds were mixed with each other in a proper molar ratio. In the next step, the

152 mixture was stirred on a magnetic stirrer at 60°C until a homogeneous liquid was formed.
153 DES was cooled to the room temperature (RT).

154 2.2.2. Preselection of DESs based on Henry's law constant

155 The preselection of DES were prepared based on Henry's constants. Studies were
156 performed using the headspace technique combined with gas chromatography-flame
157 ionization detector (HS-GC-FID) in accordance with the procedure described in the previous
158 works [53]. Only DES that were liquids at room temperature were used for the test. Liquid
159 DES (0.5 mL) was transferred to 20-mL headspace vials to which the 0.75 µL of each BTEX
160 compound was added. The vials were then sealed and incubated at room temperature for 24
161 hours. Then 100 µL of the headspace was introduced into the gas chromatograph. The
162 concentration of BTEX in the gas phase (headspace) was determined on the basis of
163 calibration curves prepared in accordance with the procedure presented in the previous works.
164 The concentration of selected BTEX compounds in a liquid phase (DES) after headspace
165 procedure was calculated according to Eq. 1:

$$166 \quad V_1 \cdot C_0 = V_1 \cdot C_1 + V_g \cdot C_g \quad (1)$$

167 where: V_1 – DES volume [cm³];

168 V_g – gas volume (headspace volume) [cm³];

169 C_0 – initial concentration of BTEX in liquid sample (DES) [mol/m³];

170 C_1 – concentration of selected BTEX in DES phase after headspace procedure
171 [mol/m³];

172 C_g – concentration of selected BTEX in gas phase after headspace procedure
173 [mol/m³];

174

175 The dimensionless Henry's law solubility constant was calculated according to Eq. 2:

176

$$H = \frac{c_g}{c_1} \quad (2)$$

178 2.2.3. Characterization of DESs

179 DESs viscosity and density measurements were made in the temperature range from 20 to
180 50 °C. Measurements were made using the following apparatus BROOKFIELD LVDV-
181 II+viscometer (Labo-Plus, Poland), and a DMA 4500 M density meter (Anton Paar, Poland).
182 The surface tension (ST) of DES was measured using a tensiometer (A KRÜSS K9 model
183 K9MK1) in the range of temperature of 20-50°C. The tensiometer was stabilized for 30
184 minutes and calibrated using water at 20°C. Then the 4 mL of DES was placed in a
185 thermostated measuring cup. After reaching the appropriate temperature, the ST of DESs was
186 measured automatically using A KRÜSS K9 within 3 seconds. The melting point (MP) of
187 DESs was determined visually by cooling eutectic mixtures to -25°C in a cryostat (HUBER,
188 Germany). Then the temperature was increased at 1°C/min. The temperature at which the
189 appearance of the first liquid drop was observed was taken as MP. Measurements of all
190 physical properties of DES were repeated three times.

191

192 2.2.4. Mechanism of DESs formation, and BTEX absorption

193 The absorption mechanism and structural properties of new DESs were analyzed by ATR-
194 FTIR spectroscopy by means of a Bruker Tensor 27 spectrometer (Bruker, USA) with an
195 ATR accessory and OPUS software (Bruker, USA). The following parameters were adopted
196 for the studies: 4000–600 cm⁻¹; the number of background and samples scans: 256;
197 resolution: 4.5 cm⁻¹; slit width 0.5 cm. Additionally, nuclear magnetic resonance
198 spectroscopy (NMR) measurements were performed in order to receive more deep insight into
199 DES formation and the efficiency of BTEX absorption. Samples for NMR analysis were

200 prepared in 5 mm tubes by weighing 20 mg of DES and inserting 0.4 mL of chloroform-d1.
201 The NMR analysis was done out at 20°C by means of Bruker Avance III HD 400 MHz
202 (Bruker, USA).

203 For the theoretical examination of the mechanism of BTEX absorption, Conductor-like
204 Screening Model for Real Solvents model (COSMO-RS) was used. For these propose, ADF
205 COSMO-RS software (SCM, Netherlands) was used according to previous studies [40,42,54].
206 In the first stage, the geometry optimization of DES which were selected during HS-GC-FID
207 analysis including Cam:OA, Cam:DA, C-one:OA, C-one:NA, C-one:DA, C-one:Lev, Eu:OA,
208 main components of commercially available absorbent (i.e. tetraoxaoctadecane and
209 pentaohaheneicosane) and BTEX was prepared. The geometry optimization of all eight
210 absorbent complexes in 1:1 molar ratio, and BTEX compounds was performed using the
211 continuum solvation COSMO model at the BVP86/TZVP theoretical level. In order to find
212 the most stable conformers of studied compounds, optimization studies were performed in the
213 gas phase. In the next step, the vibrational analysis was performed to find conformers that
214 corresponds to the true energy minimum. The full geometry optimization of studies
215 compounds was prepared only for the most energetically favorable conformers. For all
216 absorbents, the affinity to BTEX was calculated by means of activity coefficient according to
217 Eq. (3).

$$\ln(\gamma_i) = \frac{u_i^a - u_i^p}{RT} \quad (3)$$

221 where: u_i^a – chemical potential of selected BTEX in absorbent;

222 u_i^p - chemical potential of pure BTEX compounds;

223 R - universal gas constant (8.314 J/mol);

224 T - temperature (K).

225 In order to visualize the charge distribution of absorbents and BTEX, the σ -profiles were
226 calculated using the 3D surface charge densities.

227 **2.2.5. Absorption and desorption process of BTEX**

228 In this work, the absorption/desorption set-up was described in the previous work was
229 used [42]. In the first stage, pure nitrogen was passed through a vial containing 1mL of each
230 BTEX compound. The obtained contaminated gas via bubbling phenomena was diluted with a
231 model biogas stream (CH_4 : CO_2 : N_2 in 5:3:2 volume ratio) to 2000 mg/m^3 concentration of
232 BTEX. In the next step, the biogas stream was directed into the absorption column with an
233 appropriate absorbent. The desorption process was carried out using the pure nitrogen
234 barbotage method at elevated temperatures in the range of $100\text{-}120^\circ\text{C}$ consistent with
235 previous research [55].

236 During the absorption/desorption processes, the biogas samples were collected before
237 and after introduction into the absorption/desorption column. The biogas samples were
238 analyzed by gas chromatography and sensors matrix. Biogas purification processes were
239 carried out until the concentration of BTEX in the inlet and outlet biogas were equal. In order
240 to ensure the correctness of the results, the absorption processes were repeated three times.
241 The absorption capacity (Q) was determined according to the previous studies [42]. To
242 determine the absorption capacity of the absorbent, the volumetric flow rates of individual
243 components of the gas mixture have been designated as the product of the volumetric flow
244 rate of the gas mixture and the concentration of its components. For this purpose, by means of
245 an Agilent ADM Flow Meter, the gas flow at the outlet of the absorption columns needs to be
246 measured. Values of Q were calculated using Eq. (4-6):

$$248 \quad \frac{d(m_{BTEX})}{dt} = (F_{IN} \cdot C_{IN}(t) - F_{OUT}(t) \cdot C_{OUT}(t)) \cdot \bar{\rho}_{BTEX} \quad (4)$$

249
$$m_{BTEX} = \int_0^{t_{sat}} [F_{IN} \cdot C_{IN}(t) - F_{OUT}(t) \cdot C_{OUT}(t)] dt \cdot \bar{\rho}_{BTEX} \quad (5)$$

250
$$Q = \frac{m_{BTEX}}{m_A} \quad (6)$$

251

252 where: m_{BTEX} – BTEX mass absorbed [g];

253 m_A – mass of absorbents used to obtain complete saturation [g];

254 t_{sat} – saturation time of absorbents [s];

255 C_{IN} – BTEX initial concentration in biogas [ppm v/v];

256 C_{OUT} – BTEX outlet concentration in biogas [ppm v/v];

257 $F_{IN,OUT}$ – Flow rate of the biogas at the inlet and outlet of the absorption column
 258 [m³/s];

259 $\bar{\rho}_{BTEX}$ – average BTEX density at a given temperature [kg/m³]

260 The absorptivity of BTEX was calculated using the following Eq. 7:

261
$$A = \frac{A_{IN} - A_{OUT}}{A_{IN}} \quad (7)$$

262 where: A_{IN} – initial total peak area of BTEX compounds;

263 A_{OUT} – total peak area of BTEX compounds after absorption process.

264

265 **2.2.6. Process control**

266 **2.2.6.1. Chromatographic analysis**

267 For the control of absorption/desorption process efficiency, biogas samples were
 268 analyzed by gas chromatography technique. In order to determine Henry's constants in static
 269 process and concentration BTEX in gas streams in a dynamic process, gas chromatograph
 270 Autosystem XL (PerkinElmer, USA) equipped with a capillary column an HP-5 (30 m × 0.25

271 mm × 0.25 μm) (Agilent Technologies, USA), and a flame ionization detector (GC-FID)
272 (PerkinElmer, USA) was used. The chromatographic analysis was conducted under certain
273 conditions: temperature of the oven 60°C, injection port temperature 250 °C; the injection
274 mode split 5:1, detector temperature 300°C, the carrier gas – nitrogen (flow rate: 1 mL/min),
275 amount of sample injected: 0.5 mL. For the determination of CH₄, CO₂, and N₂ in the biogas
276 stream during the absorption process, the gas chromatograph GC MG#5 (SRI Instruments,
277 USA) coupled to a thermal conductivity detector (GC-TCD), and equipped with a packed
278 column Porapak Q (80/100, 2 mm ID) (Restek, USA) was used. The following conditions
279 were used: temperature of the oven 40°C, injection port temperature 60°C, detector
280 temperature 80°C, the carrier gas – helium (flow rate: 5 mL/min), amount of sample injected:
281 2.0 mL.

282 **2.2.6.2. Chemical gas sensor**

283 In order to continuously monitor and control the absorption treatment of biogas, a matrix
284 consisting of the commercially available gas sensor was constructed. Basic information about
285 gas sensors used is shown in Table S1. The gas sensors were housed in separate PTFE
286 chambers. This approach makes it possible to prevent the emissions of organic compounds
287 into the measuring chamber and further reduces the absorption and chemical transformations
288 of the gaseous substances. Due to the dependence of the output signal from PID-A12 gas
289 sensors on variations in temperature, humidity, and atmospheric pressure, a sensor that
290 controls these parameters was placed in an additional chamber. As a result, the lack of
291 linearity of the PID output signal observed at higher concentrations can be corrected in the
292 software during data analysis. Whereas, NDIR sensors capable of monitoring the presence of
293 carbon dioxide and methane in process samples provide an analog voltage output proportional
294 to the concentration of these gases, which is simultaneously linearized and temperature
295 compensated. The constructed matrix allowed control of total BTEX concentrations in the

296 range of 0 to 6600 mg/m³ while carbon dioxide and methane concentrations were monitored
297 in the range of 0-100% by volume. The gas flow at the outlet of the absorption column was
298 measured using an Agilent ADM Flow Meter, which provides continuous, real-time
299 measurement of volumetric flow rate.

300 **2.2.6.3. Gas sensor array measurement**

301 The gas sensor array experimental setup is presented in Figure S1. Process samples were
302 collected at the inlet and outlet of the process and the bags made of TEDLAR film were used
303 for this purpose. The three-way valve (V1) made it possible to alternate between the analyzed
304 sample and the atmospheric air passing through the air filter to the measuring chamber.
305 Purified air was directed to the measurement chamber after each analysis in order to
306 regenerate the gas sensors and restore their input parameters. The flow rate of the sample and
307 air was controlled using the rotation speed of the diaphragm pump. The pulse width
308 modulation module (PWM) was responsible for regulating the supply voltage delivered to the
309 pump motor, which fluctuations directly affect the pump speed and thus the flow rate. The
310 sensor measurement was performed in the stop-flow mode: the sample flow time through the
311 sensor chamber was 30 seconds, than by closing the valve (V2) the sample was retained in the
312 chamber for another 30 seconds. Sensors signals were recorded using an analog-to-digital
313 converter and processed by means of dedicated software. All manufacturer's requirements
314 were taken into account when the electrical circuits for each sensor were prepared. The
315 created system was controlled automatically by the Arduino control module. All analyzed
316 samples were also subjected to gas chromatographic analysis, which was treated as a
317 reference method.

318 **2.2.6.4. Data analysis and processing**

319 Data analysis and other calculations were performed using RStudio Desktop (v. 1.4.1717)
320 software. Multiple linear regression (MLR) was selected as the calibration and validation
321 model for the gas sensor array. Thus, linear relationships between independent (sensor's
322 signals), and dependent (e.g. gas concentration, chromatographic peak area) variables were
323 determined for carbon dioxide, methane, and total BTEX. Also, other methods of data
324 analysis, e.g. Principal Component Analysis (PCA), Principal Component Regression (PCR),
325 Partial Least Squares Regression (PLSR) can be used effectively for this purpose, especially
326 when dealing with very complex sample matrices.

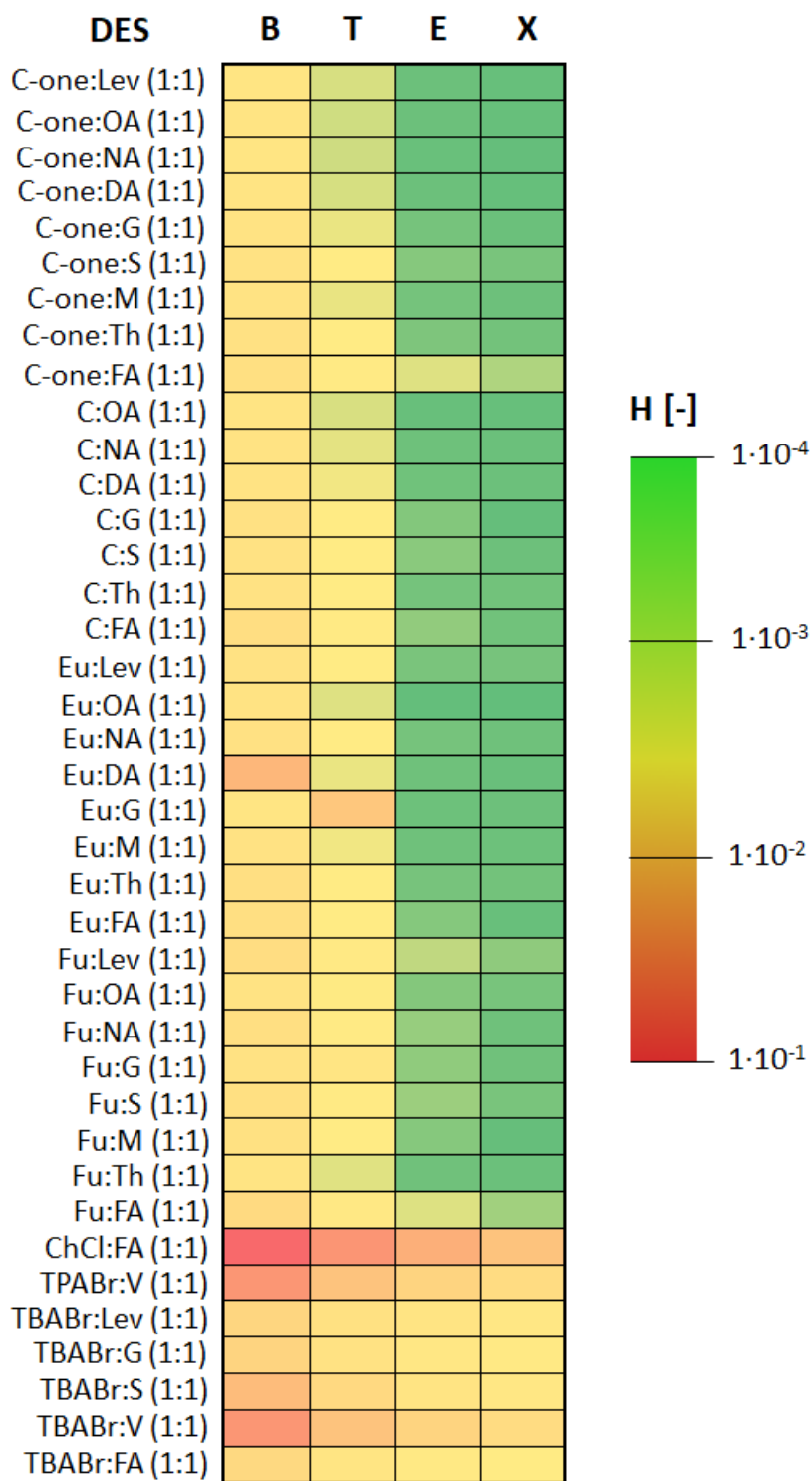
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328 **3. RESULTS AND DISCUSSION**

329 **3.1. DESs preparation and preselection**

330 In the studies, all DESs were prepared by mixing HBA, i.e., Cam, C-one, Eu, Fu, ChCl,
331 TMABr, TEABr, TPABr and TBABr, with different HBDs i.e. Lev, OA, NA, DA, DDA, G,
332 S, V, M, Th and FA in 1:1 molar ratio. From 99 tested DES, only 39 eutectic complexes
333 turned out to be liquids at room temperature. DES which met the first basic criterion of
334 absorbents - were liquids at RT, were selected for further research. Due to the relatively large
335 number of new DESs, a pre-selection of DES was performed. DES screening was performed
336 based on the determination of Henry's constants. This parameter reflects the dissolving ability
337 of BTEX in DES [56]. The obtained results are shown in Figure 1. The lower values of the
338 Henry constants (H) correspond to the greater BTEX solubility in DES. The results indicate
339 that the lowest values of H were obtained for xylene and ethylbenzene . Slightly higher values
340 were obtained for ethylbenzene and the highest for benzene. This indicates that the alkyl
341 groups form stronger non-covalent bonds with DES compared to the π interactions which is in
342 line with previous work [57]. It can be observed that BTEX compounds have the greatest
343 affinity to non-ionic deep eutectic solvents. The affinity of monoaromatic hydrocarbons to the

344 ionic ones is significantly lower. These phenomena can be explained by the occurrence of
345 very strong interaction between the cation and the anion in DES structures, that are stronger
346 than the bonds formed between the DES and nonpolar impurities [58]. The obtained results
347 suggests that ionic interactions do not play a significant role in the BTEX absorption process.
348 The most favorable results were obtained for DES consist of the monoterpenes acting as HBA
349 in combination with carboxylic acids. The lowest Henry's constant values were obtained for
350 DES consist of carvone, camphor, and eucalyptol as HBA, and carboxylic acids as HBD
351 including: C:OA (1:1), C:DA (1:1), C-one:OA, C-one:NA, C-one:DA, C-one:Lev, and Eu:OA
352 in 1:1 molar ratio. This suggests that the carboxyl group (-COOH) not only binds efficiently
353 to the carbonyl group of the monoterpenes (= O) to form strong hydrogen bonds, but is also
354 involved in the formation of strong interactions with BTEX compounds. Additionally, the
355 specific structure of monoterpenes can lead to the formation of additional π - π interactions
356 with monocarboxylic hydrocarbons. The coexistence of both types of interactions may affect
357 the high absorption capacity of the new DES. Only DES with the highest absorption potential
358 was used for further research.



359

360 **Figure 1** Henry's constants calculated for DES using the COSMO-RS model (according to the
 361 Eq. 2).

362 **3.2.Mechanism of DES formation**

363

364 Due to the synthesis of new DES, which have not been published so far, their detailed
365 structural studies were performed. In addition, understanding the interaction mechanisms
366 between HBA and HBD may play a key role in the selection of optimal absorbents for biogas
367 purification. Therefore, in this study, FT-IR analysis were performed for new DES and their
368 individual components. Figure S2 shows the FT-IR spectrum for the Eu:OA (1:1). On the
369 DES spectrum, it can be observed the shift of wide bandwidth of stretching vibrations from
370 O-H groups towards higher wavelengths (from 3002 cm^{-1} to 3014 cm^{-1}), and decreased peak
371 intensity compared with the pure HBD. In the DES spectrum, intensity decrease, and shifts
372 towards higher wavelengths are also observed for C=O stretching vibrations (from 1706 cm^{-1}
373 to 1711 cm^{-1}) and C-O-C stretching vibrations (from 1080 cm^{-1} to 1081 cm^{-1}). The obtained
374 results indicate that hydrogen bonding is formed between the carbonyl group from Eu and the
375 carboxylic group from OA. Due to the presence of active oxygen atoms (-O-, or = O) in all
376 tested HBA and carboxyl groups in HBD structures, similar band shifts can be observed in the
377 spectra of the remaining DES (Figure S3-S8). This suggests the formation of strong hydrogen
378 bonds between HBA and HBD in all tested DES [40,59].

379 In addition, ^1H NMR and ^{13}C NMR spectra were performed to confirm the formation
380 of hydrogen bonds between DES components and for the identification of potential synthesis
381 by-products. NMR spectra of Eu:OA (1:1) are presented in Figure S9, and the main shifts of
382 peaks are summarized in Table S2. In the ^1H NMR spectrum, all identified peaks correspond
383 to protons belonging to Eu and OA. This suggests that no by-products are formed during the
384 DES synthesis.

385 Additionally, characteristic shifts in the ^1H NMR and ^{13}C NMR spectra of DES in
386 comparison to pure substances can be observed. In ^1H NMR spectrum, mainly shifts toward
387 lower values can be observed. The only exceptions are the (H1) and (H5) protons with Eu for
388 which shifts towards higher values (from 2.02 to 2.19 ppm) can be observed. OA-derived

389 protons are characterized by greater shift values than protons from Eu. The largest shift can be
390 observed for the (H1) proton (from 11.60 ppm to 11.03 ppm). This is a proton from the O-H
391 group of the carboxyl group. Such a large shift (by 57 ppm) proves the direct participation of
392 this group in the formation of hydrogen bonds in DES. In the ^{13}C NMR spectrum, the shifts of
393 values for most C atoms from both HBA and HBD towards lower values can be observed.
394 Only for (C1) and (C2) from Eu, the shifts towards higher values can be observed. These
395 shifts are affected by the direct bond with the oxygen atom in the Eu molecule, which actively
396 participates in the formation of a hydrogen bond. The highest value of the shift can be
397 observed for (C1) from the OA molecule (from 180.81 ppm to 178.70 ppm). This is because
398 the C atom from the carboxyl group is involved in the formation of the hydrogen bond. NMR
399 spectra were also performed for the remaining DES. For the rest of DES, similar behavior can
400 be observed. Spectra and a list of shifts are presented in Figures S10-S15.

401 3.3. Physicochemical properties of DESs

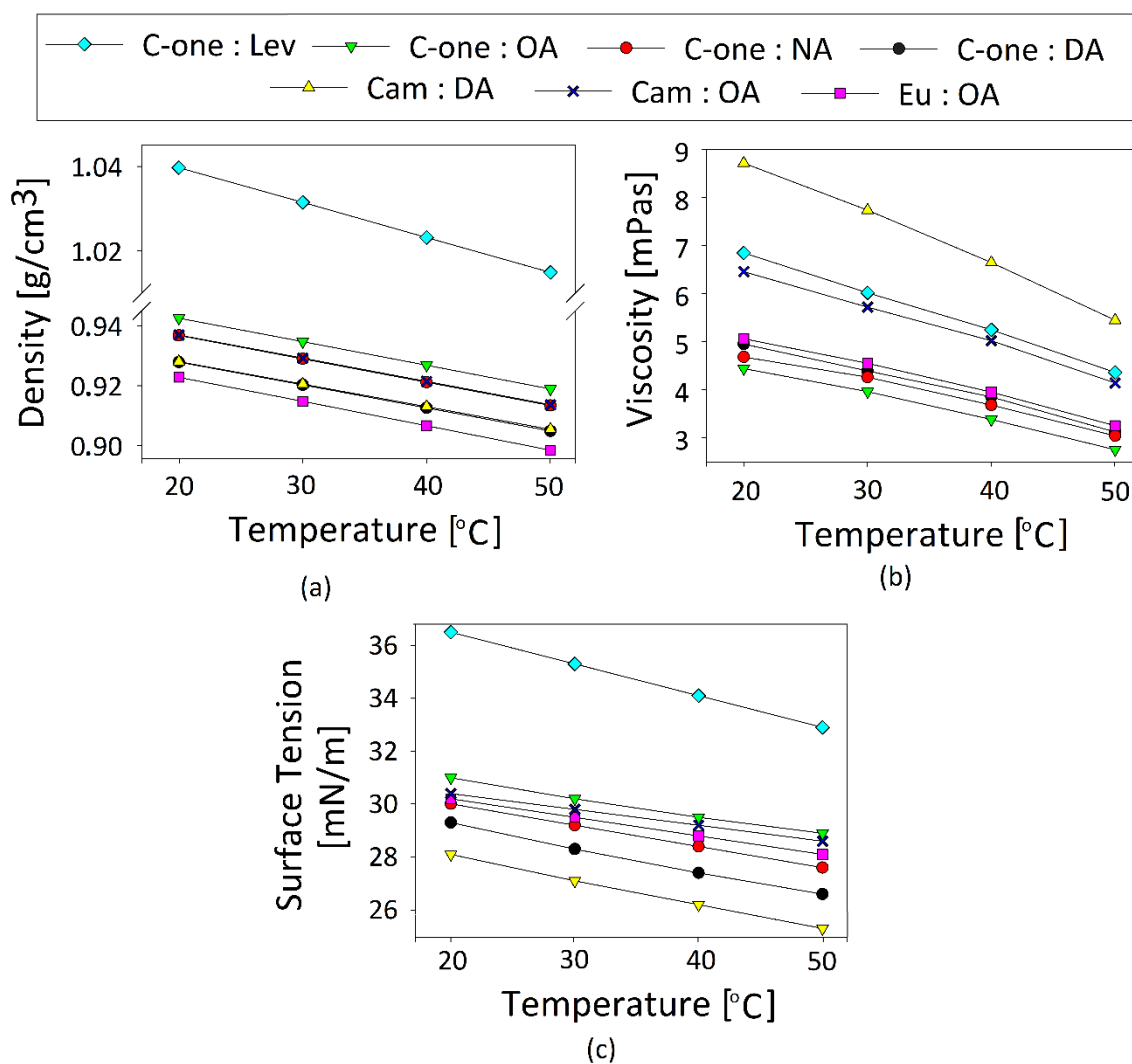
402 The practical application of DES requires knowledge of basic physicochemical properties
403 including density, viscosity, surface tension, and melting point (MP). Therefore, all listed
404 properties have been investigated in this work.

405 All studied DES are characterized by relatively significant depressions in melting point
406 compared to pure HBA and HBD. MP of pure HBAs including Cam, C-one, and Eu are
407 175°C, 25.2°C, and 1.5°C, respectively. While the MP of pure HBDs i.e. Lev, OA, NA, and
408 DA, were 33°C, 16.5°C, 12.3°C, and 31.6°C, respectively. The greatest decrease in MP can
409 be observed for C-one:Lev (1:1) which equal -25°C. Slightly lower decrease in MP can be
410 observed for the rest of DES including Eu:OA, C-one:OA, C-one:NA, C-one:DA, Cam:DA,
411 Cam:OA, which are -23, -22, -21, -19, -19, and -8°C, respectively.

412 The density of DES is a crucial parameter that significantly affects the mass transfer
413 processes. The literature data indicate that most DESs are characterized by higher density than

414 that of water, in the range of 1.00-1.35 g/cm³ at 20°C [34]. The densities of the tested DES are
415 within the range of 0.9228 - 1.0397g/cm³ at 20°C. The density values of studied DES follows
416 the order: C-one:Lev (1:1) > C-one:OA (1:1) > Cam:OA (1:1) > C-one:NA (1:1) > Cam:DA
417 (1:1) > C-one:DA (1:1) > Eu:OA (1:1). It can be observed that the density of DES closely
418 depends on the alkyl chain length of the carboxylic acids. An increase in the length of the
419 carboxyl chain causes the increase in molar volume, which affects the decrease in the density
420 value [60]. In addition, the density of DES strongly depends on temperature. The increase in
421 temperature of eutectic mixtures affects the increase in the kinetic energy of the DES
422 components, which causes a DES density decrease [61,62]. The densities of all tested DES at
423 20 – 50 °C are shown in Figure 2a.

424



425
 426 **Figure 2** The (a) density, (b) viscosity, and (c) surface tension (ST) of DESs in the
 427 temperature range of 20-50°C.

428 The next important property of absorbents is dynamic viscosity due to their strong
 429 influence on the mass transfer processes. Most DES are characterized by relatively high
 430 viscosity (>100 cP) [25,26,63], which significantly limits their usefulness in absorption
 431 processes. All tested DESs have lower viscosities than 10 mPas, and the value at 20°C
 432 follows the order: Cam:DA (1:1) > C-one:Lev (1:1) > Cam:OA (1:1) > Eu:OA (1:1) > C-
 433 one:DA (1:1) > C-one:NA (1:1) > C-one:OA (1:1). This indicates that all DES can be
 434 successfully used for absorption. Obtained results indicate that the viscosity depends on the

435 structure of both HBA and HBD. It can be observed that the viscosity of DES increases with
436 the increasing length of the alkyl chain. This is in line with previous studies [64]. The higher
437 viscosity value of C-one:Lev (1:1) compared to C-one:OA (1:1), C-one:NA (1:1), C-one:DA
438 (1:1) can be explained by the additional carbonyl group in Lev structure. In addition, Fan et
439 al. proved that the lifetime of the hydrogen bond also influences the viscosity value, which
440 decreases in DES systems where HBA belongs to monocyclic unsaturated terpene ketones
441 [65]. The conducted research confirmed the theory of Fen et al. The lowest viscosity values
442 were obtained for DES in which HBA was Carvone, which belongs to the group of terpene
443 ketones. In addition, a close dependence of DES viscosity on temperature can be observed. As
444 the temperature increase, the viscosity of DES decreases, which can be described by the
445 Arrhenius or Vogel-Fulcher-Tammann model. This indicates the standard behavior of
446 Newtonian liquids which can be explained by an increase in the average speed of DES
447 molecules in the liquid phase at higher temperatures, which decreases the intermolecular
448 forces. This causes a reduction of resistance of the fluid to flow and changes the viscosity
449 [66]. Examined DES viscosity values at 20 – 50°C are presented in Figure 2b.

450 Another examined property of new DESs is surface tension (ST). This is another
451 parameter that has a decisive effect on mass transfer process [67]. The surface tension of
452 DESs strongly depends on many factors, such as the temperature, type, and nature
453 (hydrophobic or hydrophilic) of HBA and HBD. Knowledge of ST provides important
454 information about the molecular influence on the interactions in a mixture [68]. In this study,
455 the ST of DES was measured in the temperature range of 20-50°C (Figure 2c). Typically ST
456 of DES is in the range of 40 - 65 mN·m⁻¹ at 25°C [69,70]. Experimental results indicate that
457 the ST of studied DES composed of Carvone or Camphor as HBA and various carboxylic
458 acids as HBD in a 1:1 molar ratio decreases with the increasing length of the HBD chain. This
459 is probably due to the fact that with the increasing length of the acids chain the charge density



460 decrease thus decrease the importance of electrostatic interactions between HBA and HBD. In
461 addition, the obtained results show that the ST of all DES decreases with the increase in
462 temperature. This is in line with the typical behavior of the liquids [68]. As the temperature
463 increases from 20°C to 50°C, a decrease in the ST value can be observed for C-one:Lev (1:1)
464 from 36.5 mN/m to 32.9 mN/m, while for Cam:DA (1: 1) from 28.1 mN/m to 25.3 mN/m.
465 This is due to the fact that increasing the DES temperature increases the molecular movement,
466 the average kinetic energy, and reduces the forces of cohesion between molecules (weakening
467 of the interaction between the HBA and HBD in DES) which causes the decrease in ST value
468 [71,72].

469 **3.4.Absorption of BTEX**

470 One of the key factors which have a decisive effect on the absorption efficiency of BTEX
471 is a type of DES. Therefore a DES pre-selection was performed. For this purpose, the
472 absorption processes were carried out under optimal conditions obtained in previous studies
473 [39,44]. The procedures for collecting data from sensors and gas chromatography are included
474 in the S.1. - Supplementary Materials (Figure S16 - S17 and Table S3).

475 In the preselection studies, the only variable was the type of DES, and the other
476 parameters were constant, i.e. temperature 25°C, biogas pressure 10 kPa, the volume of DES
477 50 mL, biogas flow rate 50 mL/min, and initial concentration of BTEX 2000 mg/m³. The
478 initial concentrations used were higher than the BTEX content in the biogas stream. However,
479 the concentration was adjusted to the content of all aromatics compounds in the biogas, which
480 is between 35 and 1731 mg/m³ [74]. An inert gas - nitrogen was used as the gas matrix to
481 exclude other interactions resulting from affinity to other biogas components. The
482 experimental breakthrough curves of seven different DESs are presented in Figure 3. The
483 obtained results indicate that the absorption capacity of BTEX depends both on the type of
484 HBD, HBA, and the structure of BTEX. Based on a comparison of various DES composed of

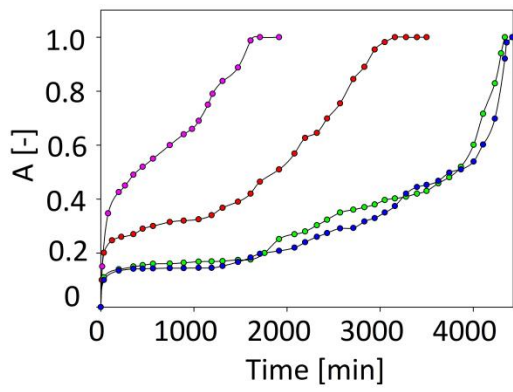
485 octanoic acid as HBD and different HBA, it can be observed that the absorption efficiency is
486 ordered as follows, Eu > C-one > Cam. The time of effective absorption is 5852, 5556, and
487 4382 min for Eu:OA, C-one:OA, and Cam:OA, respectively. This order is due to the π - π
488 interaction between aromatic groups of HBA and BTEX. In addition, the C-one and Cam
489 contain in their structure the double bond of the carbonyl group that reduces structural
490 availability and reduces the hydrophobic nature of DES, which negatively affects the
491 effectiveness of the absorption process [75]. On the other hand, based on the comparison of
492 the efficiency of the absorption with the use of DES composed of carvone as HBA and
493 various carboxylic acids as HBD, the following sequence can be observed C-one:DA > C-
494 one:NA > C-one:OA > C-one:Lev. This is probably due to the fact that increasing the alkyl
495 chain length of the HBD affects decreases the polarities of DESs. The highly nonpolar nature
496 of DES has a positive effect on the rate and capacity absorption of BTEX [76]. The absorption
497 capacity is ordered according to the following sequence of BTEX: xylene > ethylbenzene >
498 toluene > benzene, which is consistent with a growing number of methylene groups in the
499 ring of impurities. The differences between breakthrough patterns can be explained by the
500 different interaction forces between BTEX and DES, as well as the physical properties of
501 selected absorbents. Benzene is mainly able to the formation of π interaction with the DES
502 functional group including $-\text{COOH}$, $-\text{CH}_3$, $=\text{CH}_2$, $-\text{O}-$, or $=\text{O}$. However, the strength of these
503 interactions is similar in each case [77]. Therefore, it can be assumed that the changes in the
504 breakthrough curves of benzene are caused by the physical properties of DES. A comparison
505 of benzene breakthrough curves shows a close dependence of DES supersaturation on their
506 viscosity. As viscosity increases, DES is supersaturated faster, which is due to the hindrance
507 of mass exchange. However, compounds that contain additional methyl or ethyl groups can
508 form both π and other weak hydrogen bond interactions with carbonyl, ester, or carboxylic
509 groups. As observed in previous studies, the strength of the weak hydrogen bonds (i.e. C-



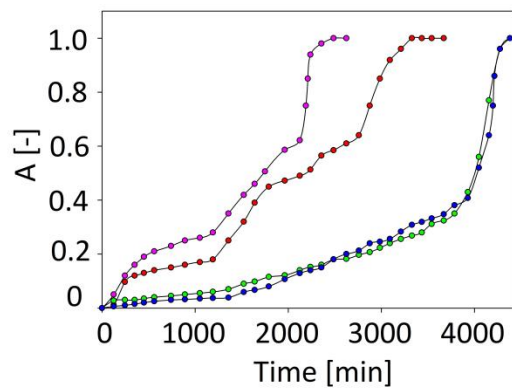
510 H···O) interaction increases with the length of the alkyl chain in hydrocarbons. This indicates
511 that the methyl groups are actively involved in the formation of non-covalent bonds with
512 DES, which is in line with the results obtained from Henry's constants and with previous
513 works [57,78]. However, differences in the saturation points of DES indicate that the basic
514 physical properties, i.e. the dynamic viscosity of the absorbents, also can affect the absorption
515 efficiency of T, E, and X.

516 DES composed of Eu and OA in a 1:1 molar ratio is characterized by the highest
517 absorption capacity. This proves that not only the structure of DES components and the
518 strongly hydrophobic nature of DES affects the efficiency of BTEX absorption, but also the
519 physicochemical properties i.e. low viscosity, high surface tension, and relatively low melting
520 point. Both types of parameters play a significant role in the absorption process and it is
521 difficult to clarify which one is more important. However, the combination of favorable
522 physical properties with the specific structure of Eu:OA enhances the effect of DES
523 absorption capacity. Therefore, further research was only done for the most favorable DES.

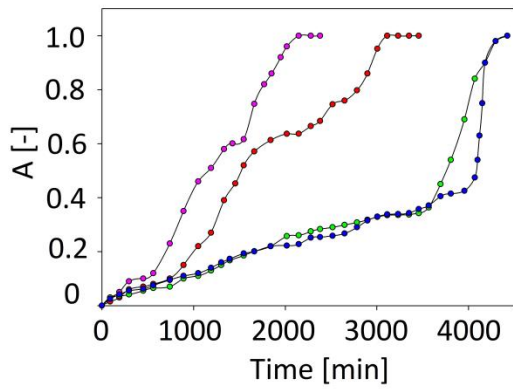
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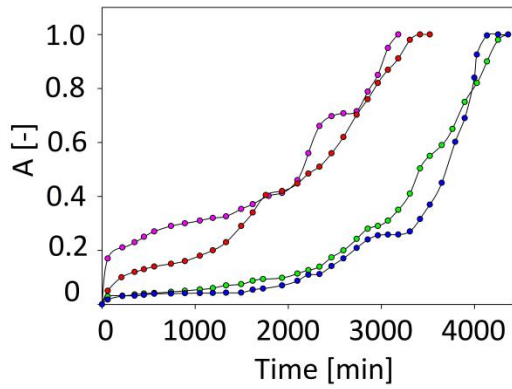
(a)



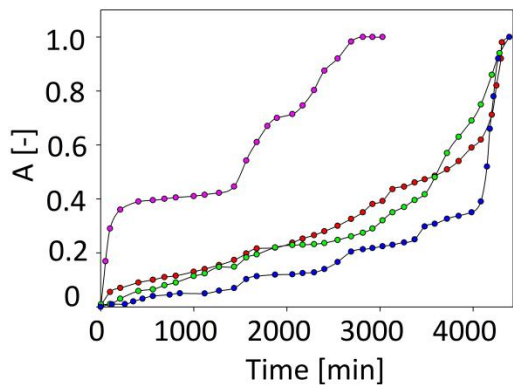
(b)



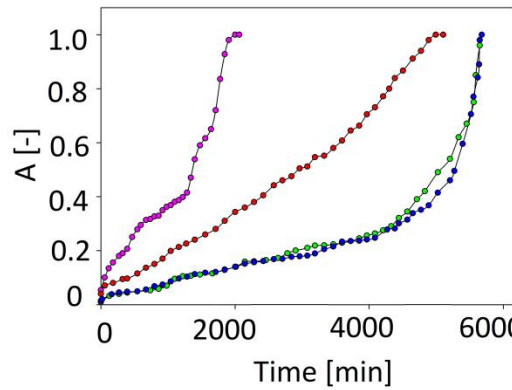
(c)



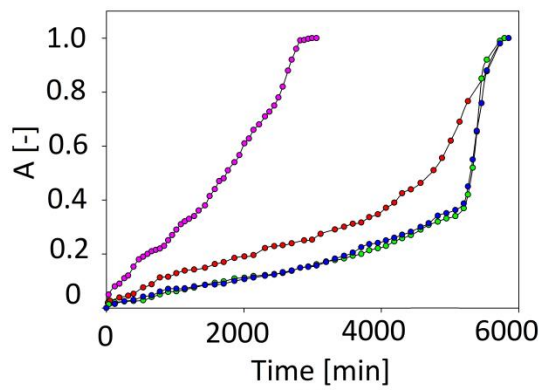
(d)



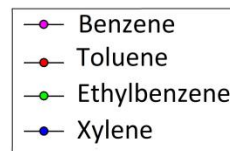
(e)



(f)



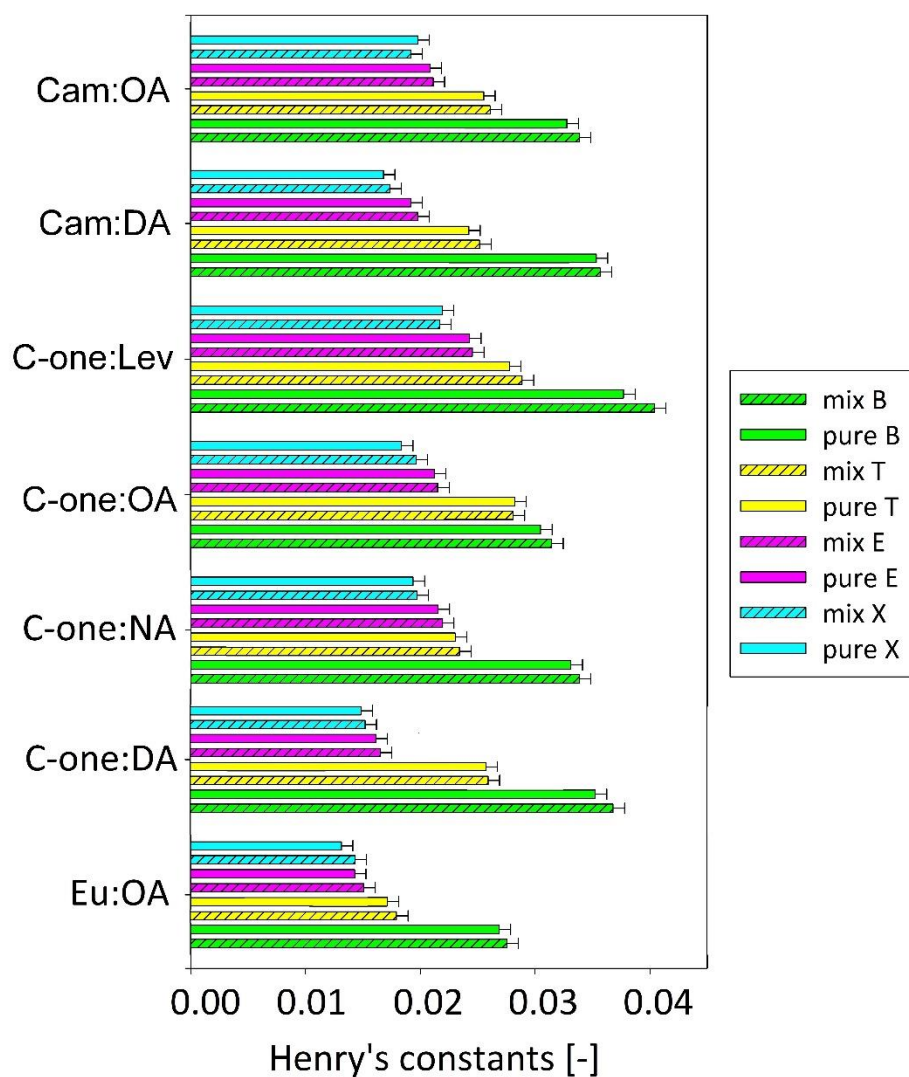
(g)



526 **Figure 3** Experimental breakthrough curves of (a) Cam:DA (1:1); (b) Cam:OA (1:1); (c) C-
527 one:Lev (1:1); (d) C-one:OA (1:1); (e) C-one:NA (1:1); (f) C-one:DA (1:1); (g) Eu:OA (1:1);
528 on different DESs (temperature 25 °C; biogas (matrix gas N₂) flow 50 mL/min; inlet BTEX
529 concentration 2000 mg/m³); the volume of the DES 50 mL; absorption column dimensions:
530 height 10 cm and width 3 cm.

531 As observed in previous work, the presence of other substances in the gas can
532 significantly affect the absorption capacity of DES. Therefore, a quick comparison of Henry's
533 constants (according to the Eq. 2) was performed for the absorption of single impurities and
534 the entire BTEX mixture from biogas under static conditions. The outcomes are shown in
535 Figure 4. The obtained results in the two variants are only slightly different from each other.
536 This indicates that the coexistence of all BTEX in the biogas stream only slightly affects the
537 absorption efficiency. This phenomenon can be explained by the lack of significant
538 differences in the structures of all monoaromatic hydrocarbons, which could combine with
539 functional DES groups and form competitive interactions.

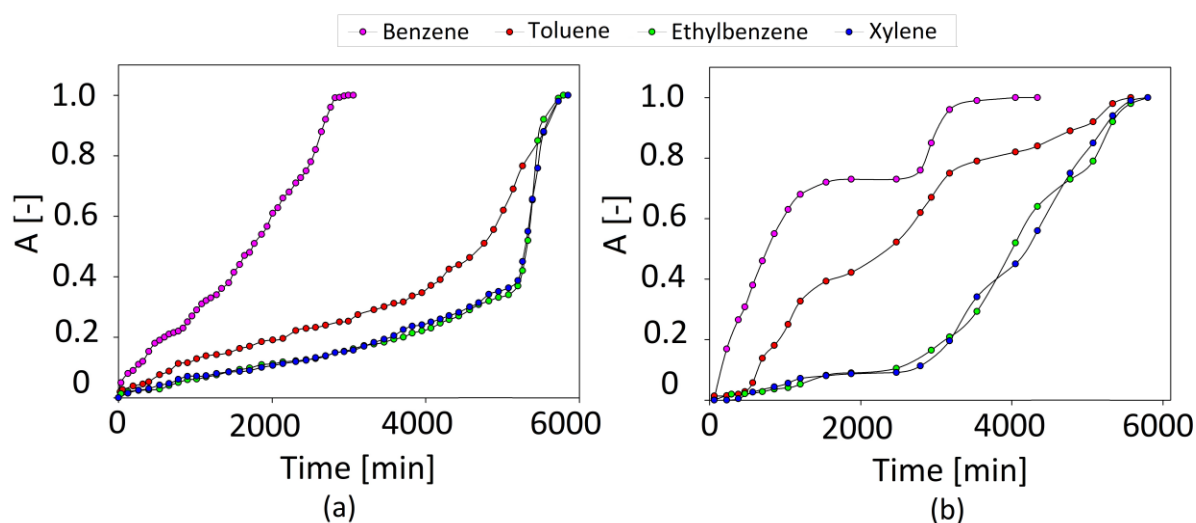
540



541
 542 **Figure 4** Henry's constants of the single impurities (solid column) and the BTEX mixture
 543 (hatch column) in DES. The total concentration of each of the impurities was 2000 mg/m^3 , at
 544 25°C .

545 In the next part of the studies, the influence of the matrix effect on the DES absorption
 546 efficiency has been investigated (Figure 5). The BTEX absorption efficiency from pure
 547 nitrogen and from a model biogas mixture consisting of methane: carbon dioxide: nitrogen in
 548 a 5:3:2 volume ratio was compared. The composition of the model biogas mixture represents
 549 a typical matrix of real biogas streams [79]. The obtained results indicate that the type of gas
 550 matrix affects the effective time of BTEX absorption. It can be noticed that the use of a model

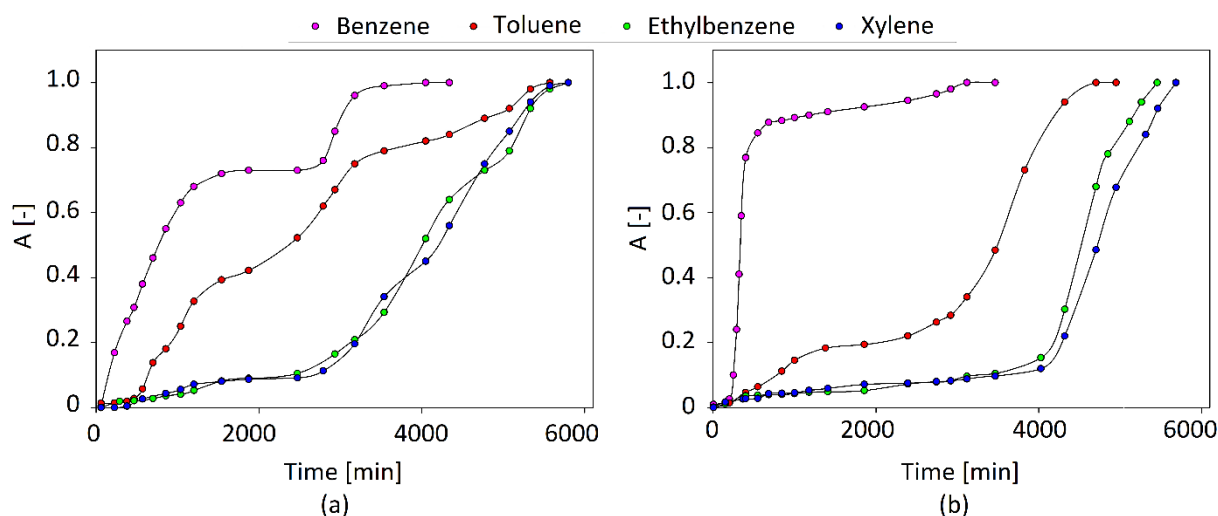
551 biogas stream reduces the absorption time and thus reduces the DES absorption capacity. This
 552 is due to the partial absorption of the main components of the biogas, i.e. CH₄ and CO₂. All
 553 tested DES are consist of HBA and HBD. Therefore, it is very likely that methane can easily
 554 bind to the hydrogen bond acceptor (CH₄···HBA), while carbon dioxide can easily bind to the
 555 hydrogen bond donor (CO₂···HBD), through non-covalent bonds [80]. Thus, competitive
 556 interactions can form that reduce the efficiency of BTEX uptake.



557
 558 **Figure 5** Experimental breakthrough curves of (a) Eu:OA (1:1) from pure nitrogen; (b)
 559 Eu:OA (1:1) from a model biogas mixture (CH₄:CO₂:N₂ 5:3:2 volume ratios) flow 50
 560 mL/min; temperature 25°C; inlet BTEX concentration 2000 mg/m³, the volume of the DES 50
 561 mL; absorption column dimensions: height 10 cm and width 3 cm.

562 In addition, the most favorable DES was compared with commercially available absorbent
 563 which is mostly consist of tetraoxaoctadecane and pentaoxaheneicosane. The obtained results
 564 are presented in Figure 6. The absorption processes were carried out using the model biogas
 565 mixture consisting of CH₄: CO₂: N₂ in a 5:3:2 volume ratio. The obtained results indicate that
 566 the new DES has an absorption capacity similar to that of a commercially available absorbent.
 567 The shortest impurities absorption time was obtained for the benzene, which was 4048

568 minutes. In turn, the longest time was obtained for the toluene, ethylbenzene, and xylene,
 569 which were 5334, 5790, 5800 minutes, respectively. The same BTEX removal trend can be
 570 observed for commercial absorbent. This indicates that the new DES may be a good
 571 alternative to commercially available sorbents. For which the shortest absorption time was
 572 achieved for benzene (3118 min). On the other hand, the absorption time was extended in the
 573 order of toluene, ethylbenzene and xylene, 4319, 5731 and 5859 min, respectively.



574
 575 **Figure 6** Experimental breakthrough curves of (a) Eu:OA (1:1) and (b) Genosorb
 576 (temperature 25°C; biogas (matrix gas: CH₄:CO₂:N₂ 5:3:2 volume ratios) flow 50 mL/min;
 577 inlet BTEX concentration 2000 mg/m³), the volume of the sorbent 50 mL; absorption column
 578 dimensions: height 10 cm and width 3 cm.

579 3.5. Mechanism of BTEX absorption

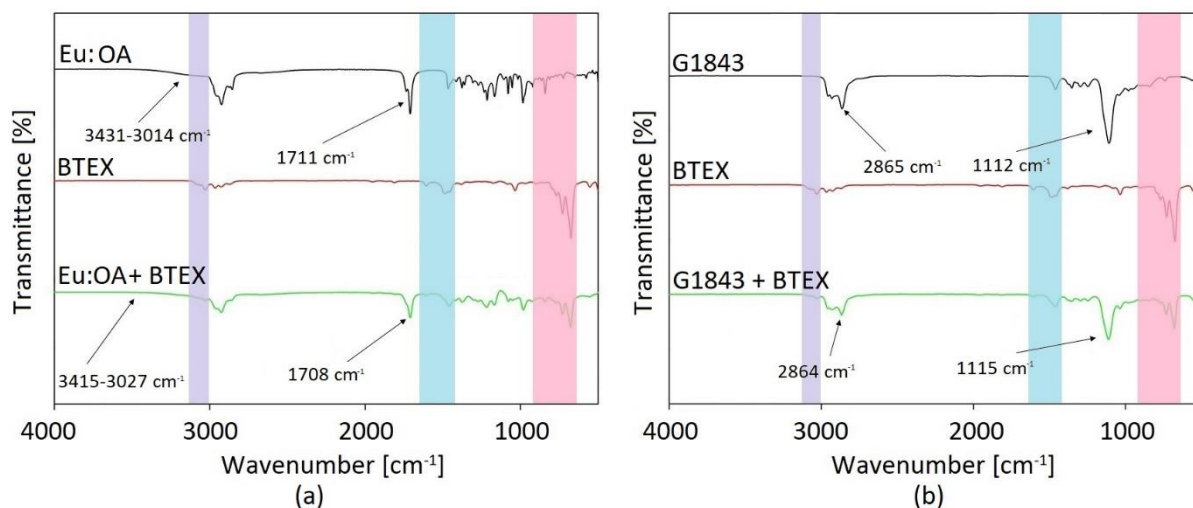
580 The absorption efficiency was also controlled at the structural level in order to explain the
 581 BTEX attachment mechanism for absorbents (DES and commercially available absorbent).
 582 For this purpose, the FT-IR and NMR analyses were carried out. Figure S18 show FT-IR
 583 spectra of the Eu:OA (1:1) and Genosorb before and after the absorption process. The
 584 mechanisms of BTEX absorption were also explained for the rest of tested DES. The results

585 are presented in Figures S19-S49. On the Eu:OA (1:1) spectrum after absorption process, the
586 characteristic peak from BTEX can be observed. The biggest changes are visible in the range
587 of 3123-3000 cm^{-1} (purple area), which can be assigned to the $\text{C}_{\text{Ar-H}}$ stretching vibrations
588 occurring in the aromatic ring. In addition, the structural changes in DES after the BTEX
589 absorption process is also in the range 1631-1420 cm^{-1} (blue area), and 907-633 cm^{-1} (pink
590 area). These changes are due to the emergence of the stretching vibrations $\text{C}=\text{C}$ and the
591 deformation vibrations outside the plane $\text{C}_{\text{Ar-H}}$, respectively. The above described mentioned
592 chemical shifts suggest that the main driving force behind the BTEX absorption process is the
593 formation of hydrogen bonds between DES and the aromatic ring with BTEX. This fact is
594 also confirmed by the shifts signals with DES corresponding to the -OH groups from HBD
595 and $\text{C}=\text{O}$ from HBA, which are shifted towards the lower wavenumbers, from 3431-3014 cm^{-1}
596 to 3415-3027 cm^{-1} and from 1711 cm^{-1} to 1708 cm^{-1} . For the remaining tested DES, very
597 similar shifts can be observed.

598 The similar results can be observed for commercially available absorbent. The
599 characteristic signals from BTEX are observed in very close ranges. In the spectrum after
600 absorption process the following signals can be observed $\text{C}_{\text{Ar-H}}$ stretching vibrations in the
601 range of 3123-3000 cm^{-1} (purple area), stretching vibrations $\text{C}=\text{C}$ 1631-1420 cm^{-1} (blue area),
602 deformation vibrations outside the plane $\text{C}_{\text{Ar-H}}$ 907-633 cm^{-1} (pink area). The peak from the
603 C-O-C bond which are visible at the wavenumber of 1112 cm^{-1} on spectrum before absorption
604 is shifted towards higher values (Figure 7). This proves that ether group participates in the
605 attachment of BTEX to the absorbent. It can be concluded that there are absorbent-BTEX
606 bonds between the ether group (from Genosorb) and the aromatic group (from BTEX), which
607 are the driving force behind the BTEX absorption process.

608





609
610 **Figure 7** FT-IR spectrum before and after BTEX absorption for (a) Eu:OA (1:1) and (b)

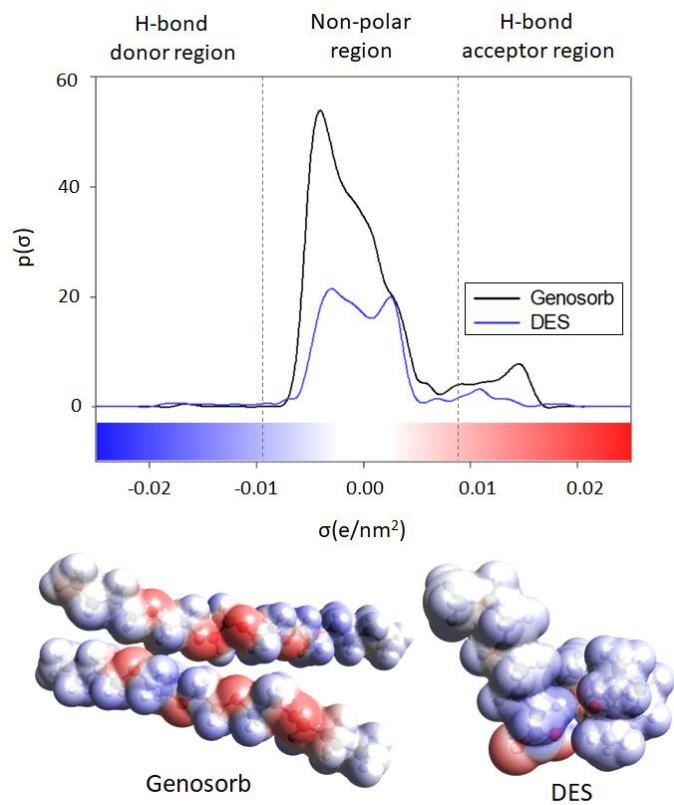
611 Genosorb.

612 In the ^1H NMR and ^{13}C NMR spectra of both Eu:OA (1:1) and Genosorb after the
613 absorption process all visible peaks can be assigned to specific atoms derived from the Eu:OA
614 (1:1) and BTEX (Figure S50). This confirms that the absorption process is a physical one,
615 without the formation of other substances by the reaction. In the ^1H NMR and ^{13}C NMR
616 spectrum for Eu:OA (1:1) after the absorption process can be observed the shifts towards the
617 higher values. For HBD the biggest differences in the NMR spectrum can be observed for
618 protons (H1) and the carbon atom (C1), which are derived from the carboxyl group the
619 octanoic acid. The described differences are at the levels 0.48 ppm and 0.9 ppm. In the case of
620 HBA, the biggest differences can be observed for protons (H6), which come from the methyl
621 group in close contact with the O atom, and the carbon atom (C6) which forms a $-\text{CH}_3$ group
622 connected to an aromatic ring. The described differences signals are at the levels of 0.34 ppm
623 and 0.46 ppm. This indicate that the interactions between BTEX and DES are mainly caused
624 by the van der Waals forces between the aromatic ring and the carboxyl group of HBD.
625 Similar behavior can be observed for Genosorb. All peaks in NMR spectra are shifted towards
626 the higher values. Detailed values of chemical shifts for Eu:OA and Genosorb are presented in
627 Table S4.

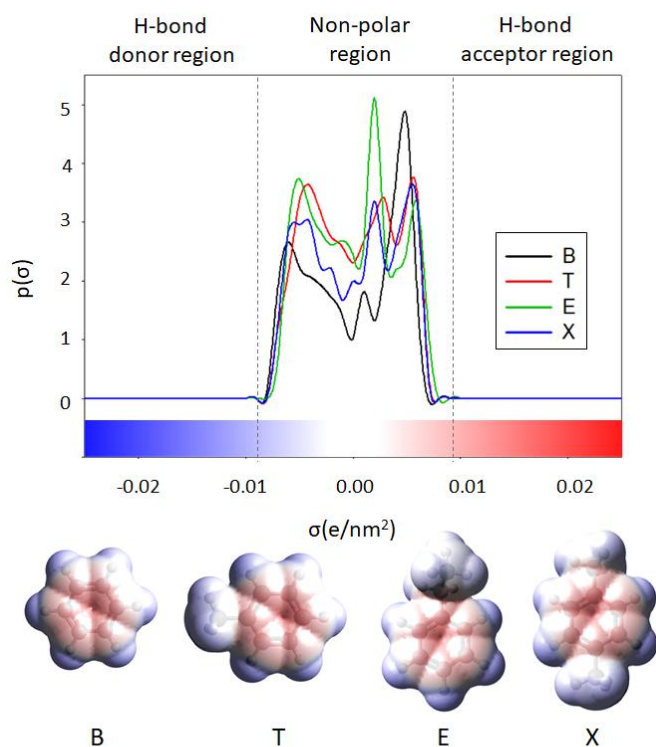
628 In order to understand the electrostatic interactions between absorbents and BTEX, σ -
629 profiles were calculated. According to the definition, σ -profiles is a distribution function that
630 relates the surface area of a molecule to the charge density of the surface [81]. Based on
631 profiles results, it is possible to predict how the BTEX molecules will interact in an absorbent
632 solute system, as well as the selectivity and solubility of BTEX in absorbents. In these studies,
633 the generated σ -profile diagrams were divided into three regions. The segment between -
634 $0.0082 \text{ e}/\text{\AA}^2$ and $+0.0082 \text{ e}/\text{\AA}^2$ charge density show that the studied compound readily
635 undergoes van der Waals interactions. Segments below $-0.0082 \text{ e}/\text{\AA}^2$ and above $+0.0082 \text{ e}/\text{\AA}^2$
636 indicate that the molecule represents the possibility of the formation of hydrogen bonding. For
637 all studied DES and commercially available absorbents, peaks in all segments can be
638 identified (Figure 8 and S51). However, the largest peaks are in the non-polar part and much
639 smaller peaks are located in the HBA and HBD regions. The -O- and =O groups are
640 responsible for the presence of peaks in the HBA region, and the -COOH group in the HBD
641 region. This indicates that strong hydrogen bonds were formed in DESs between the HBA and
642 HBD components. In order to confirm the obtained results, the electrostatic potential (ESP)
643 analysis was also performed. The results are presented in Figure 11 and S47 which show the
644 ESP mapped electron total density with an isovalue 0.001 au for absorbents, and BTEX. The
645 red area shows the negative potential region (-40 kcal/mol), the blue part of the surface
646 represents the positive potential area (40 kcal/mol), and the white part - is the non-polar
647 region (0 kcal/mol). In DES molecules, electropositive areas are located around the H atom in
648 $-\text{CH}_3$, $-\text{CH}_2$, $-\text{CH}$, and $-\text{COOH}$ groups. The electronegative regions are located in $-\text{O}-$, and
649 $=\text{O}$ group from HBA, and neutral regions are located in both HBA and HBD molecules
650 around carbon atoms. When DES is created, the electronegative area from HBA attracted the
651 electropositive area from HBD. Thus, strong hydrogen bonds are formed between the DES
652 components. The presence of large non-polar surfaces also indicates that additionally, weaker



653 non-covalent interactions, i.e. van der Waals interactions, are created between the DES
654 components. Similar interaction can be observed between BTEX and DES or commercially
655 available absorbent. Due to the presence of mainly non-polar regions in DES structures,
656 weaker electrostatic interactions are the most likely driving force for the absorption process.



(a)



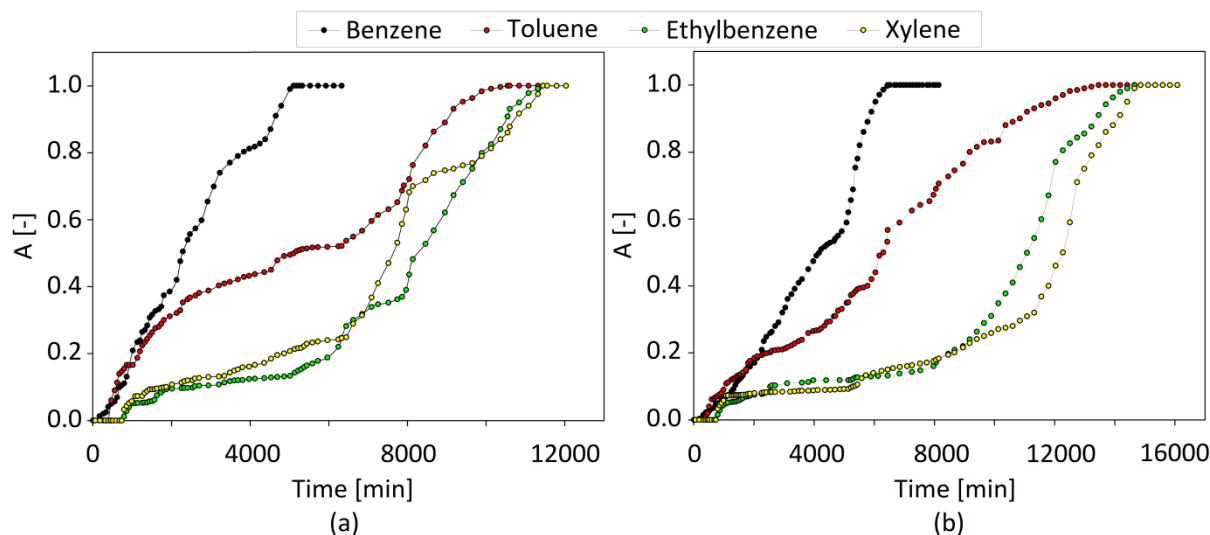
(b)

658 **Figure 8** Sigma profile and electrostatic potential maps of a) Eu:OA (1:1) and commercially
659 available absorbent; b) BTEX generated through COSMO-RS model.

660 **3.6. Increasing the scale of the absorption process**

661 For the most favorable DES, the absorption process was also performed on an enlarged
662 scale in order to confirm the usefulness of DES. The scale-up included a 10-fold increase in
663 the volume of absorbent to 500 mL and increasing gas flow rate up to 500 mL/min. The
664 processes were carried out on a model biogas stream consist of CH₄:CO₂:N₂ in 5:3:2 volume
665 ratios. The absorption process was made in two temperature variants. The first of the
666 absorption column was maintained at room temperature (RT) and the second absorption
667 column was cooled to 10°C. The absorption curves are presented in Figure 9. Based on the
668 received data, similar absorption results can be observed compared to tests performed on a
669 laboratory scale. In both processes, the order of saturation of the absorbent with aromatic
670 compounds decreases with the decreasing volatility of the compounds. Benzene in both
671 processes first breaks through the absorbent. The process of effective benzene capture is
672 almost two times shorter compared to other substances. The DES breakthrough time for
673 benzene is 5000 min and 6500 min in 25 and 10°C, respectively. The dependence of DES
674 absorption capacity on temperature is also visible for other monoaromatic hydrocarbons. The
675 duration of absorption at a temperature reduced is proportionally higher compared to room
676 temperature, for toluene from 10500 min to 13700 min, for ethylbenzene and xylene from
677 about 11500 min to 15000 min, respectively. The relationship between the increase in the
678 efficiency of the absorption process and the decrease in temperature is well known and results
679 from the exothermic nature of the absorption process [82]. Absorption curves for
680 ethylbenzene and xylene have a similar shape and a similar breakthrough time, which is
681 associated with a large chemical similarity of both compounds. In addition, it can be observed
682 that the absorption rate for less volatile compounds increases when the more volatile

683 compounds (for example benzene) have already saturated the absorbent. This is probably due
 684 to the attachment of the remaining monoaromatic hydrocarbons to the already absorbed
 685 molecules through π - π interactions.



686
 687 **Figure 9** Absorption of BTEX (a) room temperature and (b) at 10°C; absorption column
 688 dimensions: height 30 cm and width 5.5 cm

689 By integrating the areas under the obtained curves over time, the total volume of
 690 methane, carbon dioxide, and BTEX used during the process was calculated (Figure 52).
 691 Then, assuming the density of substances, their masses were determined. The sorption
 692 capacity was calculated as the ratio of the difference between the determined masses of
 693 individual compounds in the inlet and outlet streams and the mass of the absorption liquid.
 694 Additionally, the degree of absorption of gas stream components during the process was
 695 determined. All the results obtained in this way are summarized in Table 1.

696 **Table 1** Absorption capacity of DES.

Compound	Inlet stream		Outlet stream		Calculated parameters		
	V [m ³]	m [g]	V [m ³]	M [g]	Δm [g]	Capacity	Degree of

						[mg/g]	absorption [%]
Process in 10°C							
CO₂	1.3	2375	1.25	2356	18.6	40	0.78
CH₄	3.1	2132	3.1	2115	17.4	37.3	0.81
BTEX	0.011	45.3	0.0049	20.2	25.1	53.9	55.4
Process in 25°C							
CO₂	0.94	1765	0.93	1749.1	16	34.4	0.91
CH₄	2.44	1666	2.42	1654.2	12.2	26.2	0.73
BTEX	0.011	45	0.0052	21.5	23.2	49.7	51.9

697

698 The obtained results indicate that degree of BTEX absorption increase from 51.9 to 55.4%
699 with decreasing temperature from 25 to 10°C. The same tendency can be observed for
700 methane. For this molecule the degree of absorption increase from 0.73 to 0.81%. From the
701 industrial absorption processes perspective, the increase in CH₄ solubility in absorbents is
702 unfavorable, due to the fact that most industrial processes are carried out at 10°C. However,
703 the increase in methane solubility is insignificant. The acceptable solubility of methane in the
704 absorbent is 2% [83]. The opposite behavior can be observed for carbon dioxide. However,
705 the solubility of CO₂ in DES is also negligible. Therefore, it can be concluded that the
706 absorption process is selective for compounds from the group of monoaromatic hydrocarbons.

707 **3.7. Comparison of process control methods**

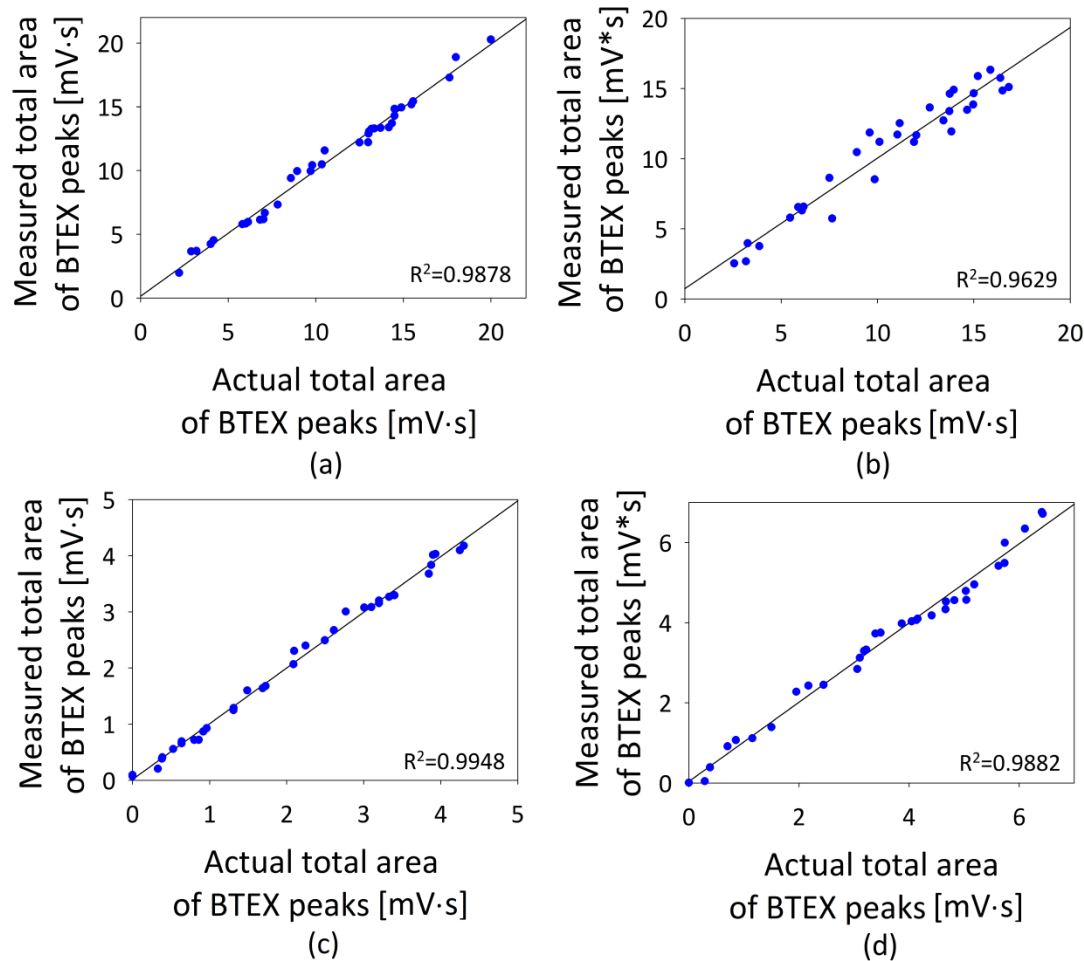
708 During the studies, two alternative methods for the control of absorption capacity were
709 tested. Instrumental (analytical) techniques and a matrix of chemical gas sensors were used
710 for process control and monitoring of tests performed. Gas chromatography with a flame

711 ionization detector (GC-FID) and thermal conductivity detector (GC-TCD) were used as a
712 reference method, which allowed qualitative and quantitative analysis of chemical compounds
713 present in the tested samples.

714 The commercially available gas sensors were selected to construct the array and based
715 on the signals received the mathematical models were developed. They show the correlation
716 between the results obtained using the reference technique and sensor matrix. The use of
717 widely available sensors makes it possible to easily reproduce the constructed array and to
718 duplicate it many times, which would be difficult to achieve in the case of testing prototype
719 sensors.

720 The prepared sensors array was calibrated and validated using Multiple Linear
721 Regression (MLR). Since the process was conducted at two different temperatures, which are
722 10°C and 25°C, it was decided to develop separate models for each of these cases. This
723 approach allowed to determine the impact of the absorption liquid components on the
724 obtained gas sensor signals. It was expected that the eucalyptol emission, which was a
725 component of the absorption liquid used, would affect the signals from the gas sensors,
726 particularly the PID sensor. For this reason, based on the recorded matrix response signals six
727 MLR models were developed: for the inlet stream (total BTEX in 10°C and total BTEX in
728 25°C) and outlet stream (total BTEX in 10°C and total BTEX in 25°C), one common MLR
729 model for carbon dioxide inlet and outlet streams and one for methane in the same
730 configuration. The MLR models for BTEX were developed to return the predicted total area
731 of the chromatographic peaks of these compounds. Correlation charts for inlet and outlet
732 streams, showing the accuracy of the prepared models, are presented in Figure 10.





733

734 **Figure 10** Actual and determined total area of chromatographic peaks correlation plot for
 735 inlet stream: (a) BTEX in 10°C , (b) BTEX in 25°C and outlet stream: (c) BTEX in 10°C , (d)
 736 BTEX in 25°C

737 For methane and carbon dioxide, model gas mixtures were prepared to reflect the
 738 expected concentrations of these gases at the inlet and outlet streams of the process. The
 739 composition of the binary gas mixtures is shown in Table S5. The gas sensor array response
 740 was recorded for each mixture, with the analysis repeated three times. The number of gas
 741 calibration mixtures prepared was 42. Correlation charts of MLR models prepared for
 742 methane and carbon dioxide are shown in Figure 15.

743 The validity of using this method is confirmed by the values of the coefficients of
 744 determination (R^2) in the correlation plots. The value of coefficients of determination between

745 chromatographic results and the values returned by prepared models are shown in Table S5.
746 For five of the six prepared models the values of R^2 were more than 0.9850. The lowest values
747 of R^2 was achieved for the BTEX inlet stream at 25°C and was equal to 0.9629, which is still
748 more than satisfactory. It should be noted that eucalyptol emission in outlet streams clearly
749 affects the signals from the PID sensor. Additionally, the emission depends on the process
750 temperature. This is shown by the intercept values in the outlet stream models. Only after
751 reduction of the matrix response to this eucalyptol the BTEX concentrations calculated using
752 the prepared MLR models are similar to those obtained by chromatographic methods.

753 The developed MLR models were used to calculate the quantitative parameter of the
754 description of the absorption process, which was absorptivity. The results of sensor matrices
755 were compared with gas chromatography, which was a reference method. Figure S53 presents
756 the absorptivity parameter determination using a gas sensor array and gas chromatography
757 throughout the process. The Root-Mean-Square Error (RMSE) for the entire range is
758 presented in Table S6. RMSE is equal to 0.017 for the BTEX in the process carried out in the
759 temperature of 10°C, and 0.067 for the BTEX absorption process in 25°C. In the case of
760 methane and carbon dioxide the mean square errors reached slightly higher values. They were
761 equal to 0.024 and 0.028 for methane in 10°C and 25°C. For carbon dioxide the calculated
762 RMSE values are very similar as they are 0.031 at 10°C and 0.039 in 25°C respectively.

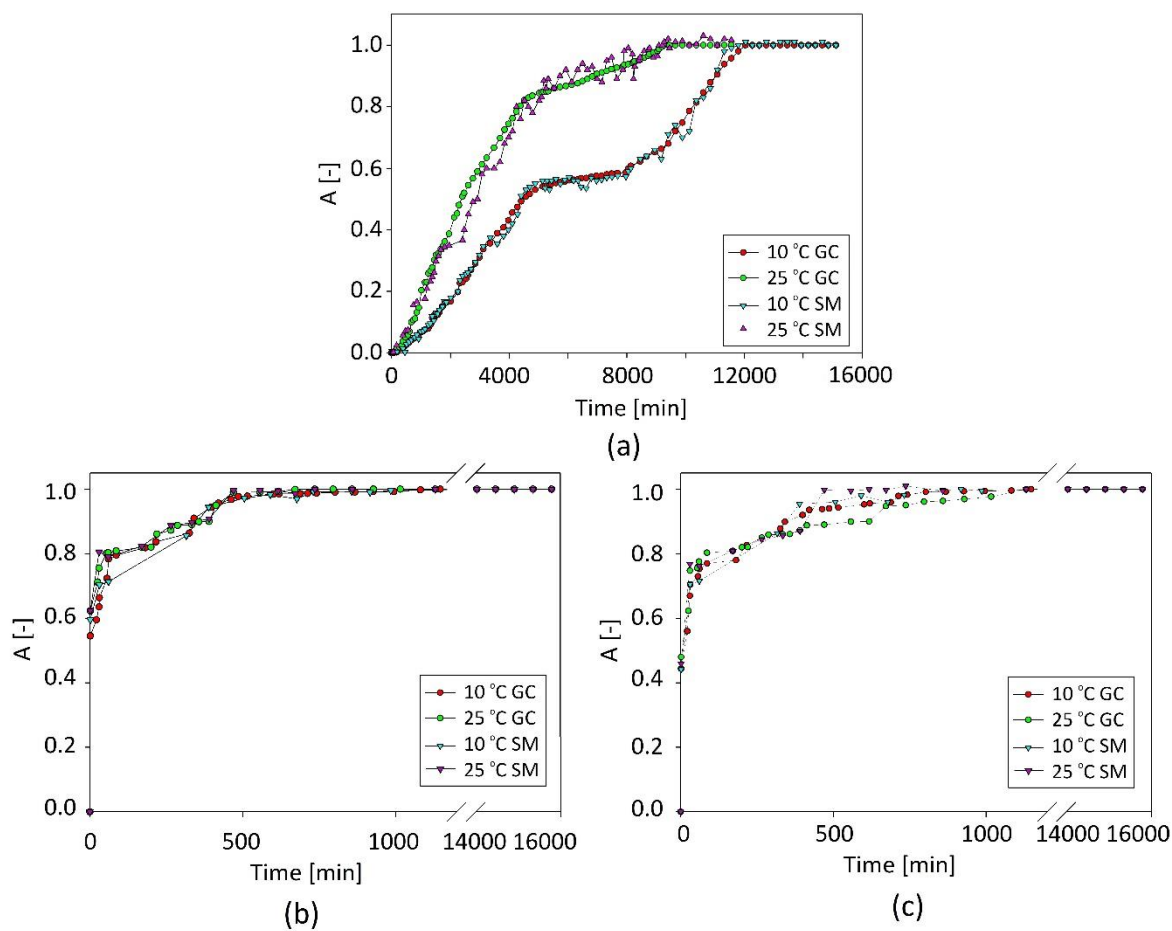
763 The obtained results indicate that the values of the total concentration of BTEX, CH₄
764 and CO₂ in biogas at the inlet and outlet do not differ significantly from this obtained using
765 reference techniques. Additionally, such results demonstrate that sensor matrices could be
766 satisfactorily used to control and monitor the absorption biogas purification processes. This
767 study confirmed that the results obtained with the gas sensor array together with an
768 appropriately selected mathematical model might be of similarly high level of quality as the
769 results obtained using the gas chromatography technique (Figure 11).

770 One of the limitations of sensor matrices is the possibility of measuring only the sum
771 of BTEX concentration. There is no possibility to receive separate signals for individual
772 compounds (inability to conduct qualitative analysis). However, from an industrial point of
773 view, there is no need to measure separate compounds. Much more important is to measure
774 the sum of impurities. A few additional challenges during sensor measurements are: the
775 influence of temperature and humidity on the stability of the sensor's signals,
776 multidimensionality of the generated signals (requires averaging by statistical methods) or
777 complicated calibration on the basis of analytical procedures and regression models.
778 Moreover, it should be noted that the research was conducted at laboratory scale. For this
779 reason, the constructed array would not be able to be used directly in the process stream, but
780 the next step will be to adapt the sensor array for operation under real conditions, e.g. using a
781 dilution module to reduce gas concentration to required ranges.

782 Chromatographic techniques are characterized by high repeatability, reproducibility
783 and accuracy and they give the possibility to identify all compounds present in a tested
784 sample. In this regard, sensor arrays are no match for the instrumental techniques but if it is
785 important to reduce the time of the analysis, investment costs or to automate the measurement
786 process, they are an excellent alternative. Ultimately, gas sensor matrixes are intended to
787 bridge the gap between gas sensors that are selective for specific chemical compounds and
788 chromatographic techniques, which have a much broader field of application but are
789 unsuitable for real-time measurements and require periodic maintenance and ensure the
790 availability of high purity gases.

791





792
 793 **Figure 11** Absorption of (a) sum of BTEX; (b) CH₄; and (c) CO₂ controlled by gas
 794 chromatography (GC) and sensory matrix (SM).

795 **3.8.Regeneration process of DES**

796 From an economic and practical point of view, regeneration of the absorbents is a crucial
 797 feature. Therefore, the DES regeneration processes after BTEX absorption were performed.
 798 The desorption process was carried out using conventional nitrogen barbotage in the
 799 temperature range 100-120°C method. Based on the obtained results, it can be observed that
 800 with the increase of the desorption temperature, the time of total BTEX removal was
 801 significantly shortened. At 120°C, complete BTEX desorption was obtained after 1 h. In order
 802 to confirm the BTEX absorption-desorption capability, DES after regeneration was subjected

803 into another absorption process. As shown in Figure S54, hydrophobic Eu:OA (1:1) retains
804 effective BTEX absorptivity at 95–97% during even ten consecutive regeneration cycles.

805 The absorption-desorption efficiency was also controlled at the structural level. Due to
806 this the ^1H NMR, ^{13}C NMR and FT-IR absorption. The results are shown in Figure S55. In all
807 spectra, the signals from the BTEX that were identified in Figure 18 have disappeared. The
808 spectra of fresh and regenerated DES are almost identical, which indicates that DES does not
809 change its structure during the desorption process.

810 3.9. Comparison of DES with other solvents

811 Currently, there are only a few studies in the literature relating to the absorption of BTEX
812 from gas. Most of the work concerns the removal of toluene using ILs or DES. The
813 comparison of DES efficiency with literature data is presented on Table 2. The obtained data
814 indicate that Eu:OA (1:1) is characterized by higher absorption capacity of monoaromatic
815 hydrocarbons in comparison to other DES, but the values are slightly lower than ILs.
816 However, the cost of producing absorbents based on ILs is many times higher than for DES.
817 In addition, the ILs have many others disadvantages such as the complicated synthesis,
818 toxicity, and poor biodegradability. The disadvantages of ILs limit their large-scale use in
819 absorption processes.

820 **Table 2** Absorption capacity of toluene in various solvents.

Type of solvents	Abbreviation	Absorption capacity [g/g]	Gas matrix	Temperature [°C]	Price [€/kg]	Pressure [atm]	Literature
DES	Eu:OA (1:1)	0.056	model biogas (CH_4 50%, CO_2 30%, N_2 20%)	10	43	1.0	This study

DES	Eu:OA (1:1)	0.050	model biogas (CH ₄ 50%, CO ₂ 30%, N ₂ 20%)	25	43	1.0	This study
DES	LauA:DecA (1:2)	0.0035	nitrogen	30	27	n.d.	[76]
DES	Lid:DecA (1:2)	0.0023	nitrogen	30	533	n.d.	
DES	Thy:DecA (1:2)	0.0021	nitrogen	20	41	n.d.	
DES	TBPB:DecA (1:2)	0.00080	nitrogen	30	183	n.d.	
DES	DecA:OctN (1:2)	0.00068	nitrogen	30	18	n.d.	
DES	ChCl:Res (1:2)	0.00051	nitrogen	30	71	n.d.	
IL	[Bmim][NTf ₂]	0.22	air	20	1600	1.17	[84]
IL	[Dmim][NTf ₂]	0.34	air	20	6263	1.17	
IL	[Emim][Ac]	0.51	n.d.	25	1180	1	[23]
IL	[Bmim][NTf ₂]	0.15	n.d.	25	1600	1	
IL	[Bmim][Otf]	0.18	n.d.	25	1430	1	
IL	[Omim][PF ₆]	0.31	n.d.	25	7920	1	
IL	[Hmpy][NTf ₂]	0.21	n.d.	25	11860	1	
IL	[EMIM][BF ₄]	0.12	synthetic air (21% O ₂ and 79% N ₂)	25	1330	1	[85]
IL	[BMIM][BF ₄]	0.24	synthetic air (21% O ₂ and 79% N ₂)	25	929	1	
IL	[HMIM][BF ₄]	0.38	synthetic air (21% O ₂ and 79% N ₂)	25	16800	1	
IL	[BMIM][I]	0.17	synthetic air (21% O ₂ and 79% N ₂)	25	5600	1	
IL	[BMIM][PF ₆]	0.29	synthetic air (21% O ₂ and	25	2276	1	

			79% N ₂)				
IL	[BMIM][HSO ₄]	0.070	synthetic air (21% O ₂ and 79% N ₂)	25	1250	1	
IL	[BMIM][CH ₃ COO]	0.40	synthetic air (21% O ₂ and 79% N ₂)	25	1380	1	

821

822 4. CONCLUSIONS

823 Deep eutectic solvents based on monoterpenes were successfully synthesized and
824 applied for BTEX absorption from the biogas stream. The most important structural and
825 physicochemical parameters that affected absorption efficiency were carefully studied. The
826 obtained results indicate that DES consists of monoterpenes and carboxylic acids that are able
827 to form strong hydrogen bonding and other weaker non-covalent interaction between active
828 groups from HBA and HBA. The result of the interaction is the formation of stable eutectic
829 mixtures, with a much lower melting point compared to pure ingredients, and favorable
830 physicochemical properties, i.e. viscosity, density, and surface tension. From the tested DES,
831 E:OA (1:1) is characterized by the highest absorption capacity of compounds from the BTEX
832 group. This is due to the combination of its favorable physicochemical properties and the
833 specific structure which selectively captures monoaromatic hydrocarbons by the formation
834 van der Waals and π - π interactions between BTEX and DES. Absorption capacity depends on
835 the absorption temperature and matrix composition. BTEX absorption capacity can vary from
836 0.05 to 0.056 g/g, which is comparable to commercially available absorbents. In addition, the
837 low cost of DES production, the possibility of multiple regenerations without affecting the
838 DES structure and without a significant reduction in the absorption efficiency, make DES an
839 excellent green alternative to other absorption media.

840 Process control and monitoring was carried out using chromatographic techniques and
841 self-constructed matrix of gas sensors. The controlled parameters of the absorption biogas
842 treatment determined with the use of sensory techniques represents a similarly high level of
843 quality as the results obtained with the gas chromatography. Thus, it was confirmed that real-
844 time monitoring of absorption process is possible and there is no need to take any samples,
845 conduct periodic maintenance of chromatographs and ensuring the availability of high purity
846 gases. In other words, the analyzes showed that very similar or even identical results can be
847 obtained faster and cheaper using gas sensors array, but they do not allow quantitative
848 analysis of tested samples. We conclude that the prepared sensor array, with the use of slight
849 technical improvements, could be used on an industrial scale to supervise and control the
850 ongoing process in real time in order to automate the process analysis.

851

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855

856 **NOTES**

857 The authors declare no competing financial interest.

858

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