

DEEP EUTECTIC SOLVENTS FOR CO₂ CAPTURE IN POST-COMBUSTION PROCESSES

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ABSTRACT. CO₂ emissions represent an actual problem for the environment. Additionally, the new demands for all chemical and physical processes request to be more eco-friendly. In this work, deep eutectic solvents (DESs), a relatively new class of solvents, were used for CO₂ capture and desorption. DESs are more environmentally friendly than classical solvents. Two choline chloride-based DES – ethaline (ChCl:EG, 1:2 molar ratio) and reline (ChCl:U, 1:2 molar ratio) were prepared and characterized before studying their CO₂ absorption – desorption capacity. The formation of eutectics was confirmed by FT-IR analysis and DESs were characterized in terms of pH, density, viscosity, refractive index, and electrical conductivity. The tests showed that ethaline had better CO₂ absorption and desorption capacity than reline, which could be explained by several parameters.

Keywords: CO₂ capture, deep eutectic solvents, green solvents

INTRODUCTION

The demand for energy in the world market presents a complex transition, compartmentalized by several dimensions: geopolitical, economic, technological and climatic. These developments lead to new strategic partnerships with security, investment, trade, and technology. From the perspective of the latest EU documents, environmental security becomes the fundamental idea of sustainable development.

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The EU has already made a first step in the Spring European Council since 1990, setting an ambitious target for the whole Union, to reduce greenhouse gas emissions (GHG) by 20% by 2020. Another objective consisted in a contribution of 20% of renewable energy resources to the European Union's from the total energy consumption by 2020. In 2016 GHG emissions had a value of 88 million tons CO₂ equivalent, representing a decrease by 54% compared to the emissions of 1990 (226 Mt eq. CO₂). At present time, Romania contributes to the total GHG emissions at European Union level by approximately 2.5% of the total emissions, which is lower than in 1990 when the contribution was higher than 4% [1].

The most important contribution to climate change results from CO₂ emissions, due to the large quantities released in the atmosphere especially by the energy sector, over 30 billion tons yearly. In 2016 the CO₂ level raised 50% faster than the average in the previous decade, leading to its level rising by 45% above pre-industrial levels, i.e. the highest concentration in the last 800,000 years [2].

In 2018, 66.3% of the total world electricity production was generated by using as combustible fuels: coal and coal products, oil and oil products, natural gas, and biofuels – (i) solid biomass and animal products, (ii) gas/liquids from biomass, industrial waste and municipal waste. Worldwide, 38% of the electricity is obtained by burning coal, 23% by using natural gas, 16.2% hydropower and 10.1% nuclear power. The newer solutions (wind, solar, biofuel and waste) are used for 9.1% energy production [3]. Abruptly halting the use of fossil fuels risks leading to the collapse of the current society. Therefore, the decision was to gradually give up coal, oil, and natural gas while looking for solutions to capture CO₂ emissions from fuel processing.

Reducing the pollution generated by the fossil fuels combustion is possible through technologies such as *CCUS (Carbon Capture, Utilization and Storage)*. CO₂ could be stored at large depths, in rock layers or even in the oceans (but with high risks to the aquatic area), could be injected to extract oil or methane, and could be used, but in small amounts, in various activities (industry food, chemical, agriculture, and carbon fiber manufacturing) [4]. Another method of storage would be the natural one in the biosphere, but there is the disadvantage of slow absorption of CO₂ by plants and the need for large areas for forest rehabilitation [5]. This method, however, is seized for the storage of excess CO₂ from the atmosphere.

The CO₂ post-combustion capture is the most advanced technology that can be easily adapted to the large capacities installed in the thermoelectric power plants. The principle of the method consists in the chemical absorption of CO₂ from the flue gas using a solvent (amine or cooled ammonia) with an approximately 95% efficiency. Unfortunately, the energy penalty for chemical absorption process integration in a coal fired power plant is around 10-15 % [6].

Recently, deep eutectic solvents (DESs) were proposed as an efficient and more environmentally friendly alternative to classical methods for the absorption of post-combustion CO₂ from combustion gases [7].

DESs consist of two or three components (ideally non-toxic and cost-effective), which are associated via hydrogen bonds forming eutectic mixture with a melting point below the melting temperatures of each component in part. One of the great advantages of DESs is the possibility to tailor them so that they are specific to individual applications. Most DESs are mixed systems of Lewis or Brønsted acids and bases, generally obtained by binding quaternary ammonium salts acting as hydrogen bond acceptor (HBA) to a salt of metal or another hydrogen bond donor (HBD) [8]. There are also other possible combinations, for example between carbohydrates. Deep eutectic solvents are made up of large, asymmetric molecules, with low network energy, thus explaining the low melting temperatures. The dislocation of the electrical charge that may occur in a hydrogen bond (e.g. between a halogen ion and a donor hydrogen molecule) is responsible for decreasing the melting point of the mixture from the individual temperatures of components.

The most investigated DESs are those based on choline chloride, which is biodegradable, nontoxic, cost-effective and which can be extracted from biomass. These DESs were also found to be the most effective in CO₂ absorption. Most of the studies reported until now investigated the absorption / solubility of CO₂ in DESs [9-13]. There are only few reports dealing with CO₂ desorption from DESs and most of them are based on theoretical simulation. Experimental investigation of desorption is scarce, to the best of our knowledge.

In this paper, we set out to prepare and characterize 2 deep eutectic solvents: choline chloride: urea with 1:2 molar ratio – also called reline; and choline chloride: ethylene glycol, 1:2 molar ratio, respectively ethaline, and to determine their CO₂ absorption and desorption capacity under several conditions.

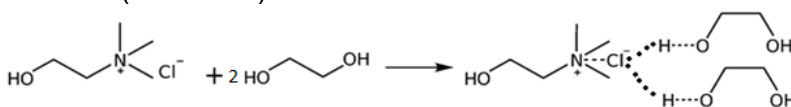
The process of CO₂ separation by absorption into DES is similar to the other solvents (ammonia, amines, etc.) [14], consisting in a typical absorber unit followed by a desorption unit configuration. A compressor pumps the CO₂-rich flue gas into the absorption column, where it meets the DES, and releases the CO₂-poor flue gas. After that, the CO₂-rich solvent is moved into the desorption column, where, using a reboiler, pure CO₂ is discharged for further utilization and/or storage, and the regenerated solvent is recycled back to the absorption unit. As operating parameters, the temperature and pressure in the two columns, the absorbent mass, the solvent regeneration energy, and the pressure required for the compressor must be taken into account.

RESULTS AND DISCUSSION

Preparation and characterization of DES

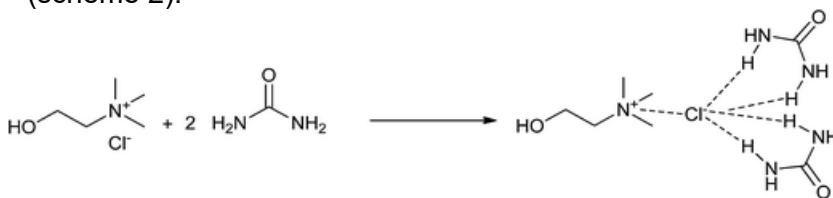
As part of a new class of solvents, the mechanism of formation of eutectic mixtures is not fully known. The following "molecular cage" structures [15] are proposed as illustrated by the schemes 1-2

- A) Choline chloride, together with two ethylene glycol molecules, forms ethaline (scheme 1).



Scheme 1

- B) Choline chloride, together with two urea molecules, forms reline (scheme 2):



Scheme 2

The change in the FT-IR spectral response between pure substances and the formed eutectic due to the physico-chemical interaction between ChCl-EG and ChCl-U is highlighted in Figure 1.

Between 3600 and 3000 cm^{-1} the vibrations of hydrogen bonds of the type O-H $\cdots$ N-H, and / or O-H $\cdots$ O and/or N-H $\cdots$ O are observed [16], which denotes the existence of molecular aggregates specific to eutectic mixtures. In the case of reline, this spectral band has a maximum at 3329-3328 cm^{-1} , specific to hydrogen bonds and a maximum at 3198-3197 cm^{-1} , specific to the -NH group. These are correlated also to vibration bands at 1660 cm^{-1} , 1656 cm^{-1} and 1607 cm^{-1} . The presence of the HO HN group from 924 cm^{-1} is also noteworthy (Fig. 1A).

Ethaline has a very wide and high intensity band, specific to intramolecular -OH bonds, and indicates the formation of new hydrogen bonds and/or molecular aggregates, with a maximum at 3321-3322 cm^{-1} . Relevant is also the formation of new hydrogen bonds with absorption band at 3035 cm^{-1} , specific to the O-H $\cdots$ N-H and/or N-H $\cdots$ O type bonds, correlated also with the vibration band at 1653 cm^{-1} . It is also worth noting the appearance of bands specific to the C-C-O- group from 1084 cm^{-1} and from 1038-1039 cm^{-1} and the HO $\cdots$ HN group from 925 cm^{-1} , (Fig. 1B).

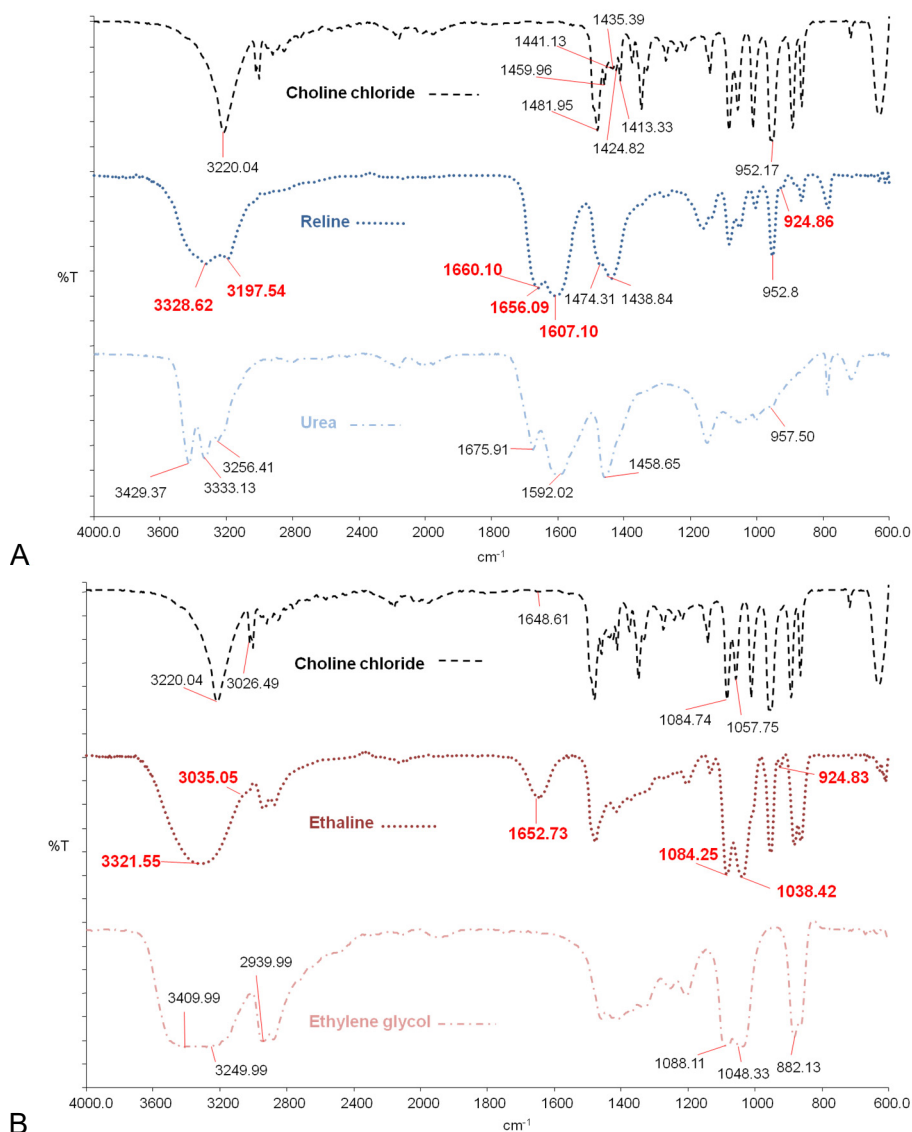


Figure 1. FT-IR spectra of reline (A), ethaline (B) and the individual components

The pH of our prepared reline was found to be moderately alkaline due to urea and that of ethaline was close to neutral. The values are similar to those of commercial DESs (Table 1) and are close to the values reported in the literature, at this molar ratio [17]. A special equipment was used, a pH-meter electrode for viscous samples from Mettler Toledo *InLab® Viscous Pro-ISM*.

Table 1. pH values of reline and ethaline samples

Sample	pH	Standard deviation
<i>Commercial reline</i>	9.74	0.0153
<i>Prepared reline</i>	9.14	0.0252
<i>Commercial ethaline</i>	7.57	0.0404
<i>Prepared ethaline</i>	7.27	0.0265

The densities were also close to the values of the commercial reline and ethaline. The density of reline was lower than reported in the literature [18], probably due to residual humidity. The results are shown in Table 2.

Table 2. Density values of reline and ethaline samples

Sample	Density g/cm ³	Standard deviation	In literature
<i>Commercial reline</i>	1.1926	0.0005	1.25 [18]
<i>Prepared reline</i>	1.1988	0.0008	
<i>Commercial ethaline</i>	1.1167	0.0007	1.12 [18]
<i>Prepared ethaline</i>	1.1186	0.0007	

Ethaline is 20 times less viscous than reline. The viscosity values obtained for our prepared DESs were similar to the commercial DESs and to the values reported in the literature (Table 3). Most eutectic solvents have high viscosities, more than 100 cP, attributed to the extensive network of hydrogen bonds, which do not allow the free movement of chemical species. Other explanations could be the large ions that give small free volumes in the structure of DES or the existence of other electrostatic forces, such as Van der Waals. High viscosity solvents would increase the cost of CO₂ absorption process and it is therefore not desirable for CO₂ capturing. In our case the difference between ethaline and reline is probably due to the higher flexibility of the ethylene glycol molecule compared to urea and the liquid character of ethylene glycol [19].

Table 3. Viscosity of reline and ethaline samples

Sample	Viscosity cP 25°C	Standard deviation	In literature
<i>Commercial reline</i>	739.7	0.7750	750 [18]
<i>Prepared reline</i>	735.5	0.5508	
<i>Commercial ethaline</i>	38.8	0.3512	37.0 [18]
<i>Prepared ethaline</i>	36.0	0.2082	

Electrical conductivity is correlated with viscosity. Reline has much lower conductivity due to its higher viscosity compared to ethaline (Table 4). Due to high viscosities, the electrical conductivity of DESs does not exceed 2 mS/cm at room temperature in general [20]. Ethaline is one of few DESs with higher conductivity, so better electron transfer which should theoretically influence the CO₂ absorption positively. Increasing the temperature should lead to an increase in electrical conductivity, as it decreases viscosity.

Table 4. Electrical conductivity – reline and ethaline samples

Sample	Electrical conductivity mS/cm	Standard deviation	In literature
<i>Commercial reline</i>	0.187	0.0031	0.2 [21]
<i>Prepared reline</i>	0.193	0.0036	
<i>Commercial ethaline</i>	7.39	0.0208	7.61 [21]
<i>Prepared ethaline</i>	7.54	0.0603	

The refractive index determined for DES samples, both commercial and prepared in this work is slightly different from the data already reported [22]. This is probably related to the experimental method used. The refractive index is a measure of the electronic polarizability and intermolecular interactions between DES components [21].

Higher refractive index of reline compared to ethaline suggests stronger interactions between choline chloride and urea than between choline chloride and ethylene glycol (Table 5). Reline is characterized by a “H-bound soup”, wherein different types of H-bond (NH...O=C; OH...O=C; OH...Cl; NH...Cl; OH...NH; CH...Cl; CH...O=C; NH...NH and NH...OH) are possible to be formed [21, 22]. Different types of complex ionic species are formed in reline, such as [Cl(urea)₂]⁻ complexed anion and urea[choline]⁺ complexed cation [22]. Most probably, these strong intermolecular interactions are responsible for the high reline viscosity.

Table 5. Refractive index – reline and ethaline samples

Sample	Refractive index	Standard deviation	In literature
<i>Commercial reline</i>	1.5035	0.0005	1.4826 [23]
<i>Prepared reline</i>	1.5034	0.0004	
<i>Commercial ethaline</i>	1.4625	0.0004	1.3326 [23]
<i>Prepared ethaline</i>	1.4635	0.0002	

CO₂ Absorption tests. The tests started with the following parameters: temperature 25°C, pressure 1-30-60 bar, flow 200 ml/min, 30 minutes, until the second flowmeter showed the same debit as the first one (fig. 2). The CO₂ absorption value is up to 6% per ethaline and 2% for reline, at the highest tested pressure, 60 bars, in line with the reported data. Slightly higher solubility of CO₂ in ethaline compared to reline was obtained by Mirza et al., at low pressure [13].

Recently, Chhotaray et al. correlated the CO₂ capture capacity to the free volume (V_f) of solvent [24]. We have also calculated the free volume of the two DESs and determined the value 117.30 cm³/mol for reline and 130.66 cm³/mol for ethaline. The higher V_f of ethaline compared to that of reline could also contribute to the higher CO₂ absorption observed for ethaline. Most probably, the stronger intermolecular interactions in reline, compared to ethaline, hamper CO₂ sorption.

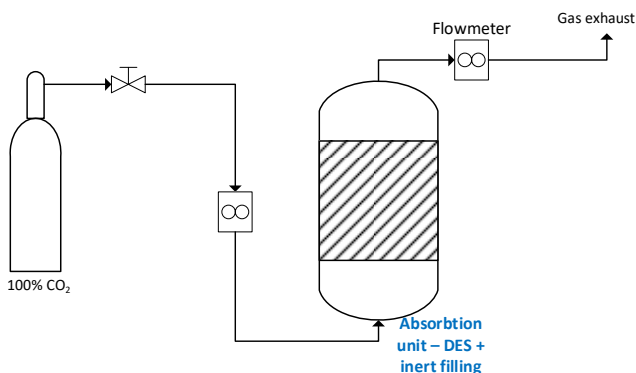


Figure 2. Absorption scheme of the scCO₂ system reactor

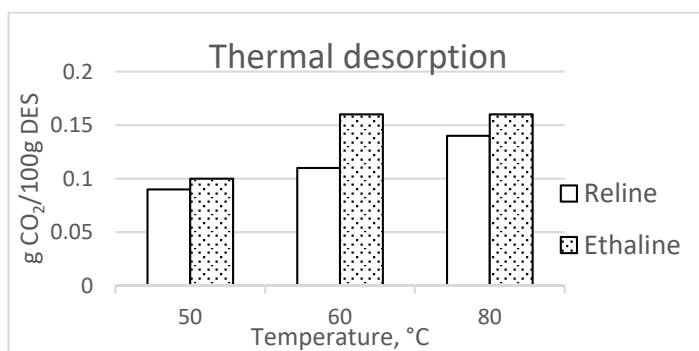
Two types of desorption methods were tested: in the vacuum oven (-0.75 bar) with heat and the classic way, thermal heating at normal pressure (1 bar). The vacuum did not help the desorption at room temperature, but it did at 60°C.

CO₂ Desorption in vacuum oven. The data are presented in Table 6. These data demonstrate that the absorbed CO₂ could be partially desorbed from the tested DES by vacuuming. Ethaline performed better than reline in sorption and desorption of carbon dioxide. For ethaline, the desorption rate could reach 3.75 g per 100 g of DES (62.5% from the solubilised CO₂, compared to only 34.5% in the case of reline after absorption at 60 bar).

Table 6. Amount of CO₂ desorbed after vacuuming at 60°C

	<i>Solvent</i>	<i>Reline</i>	<i>Ethaline</i>
Absorption at 1 bar	<i>Desorbed CO₂ mass – 100g DES</i>	0.0003	0.0024
	<i>g CO₂ / g DES</i>	0.3×10^{-5}	0.24×10^{-4}
	<i>Molar fraction</i>	2.63×10^{-6}	2.068×10^{-5}
Absorption at 30 bars	<i>Desorbed CO₂ mass – 100g DES</i>	0.23	2.12
	<i>g CO₂ / g DES</i>	0.0023	0.0212
	<i>Molar fraction</i>	0.002	0.0179
Absorption at 60 bars	<i>Desorbed CO₂ mass – 100g DES</i>	0.69 g	3.75 g
	<i>g CO₂ / g DES</i>	0.0069 g	0.0375 g
	<i>Molar fraction</i>	0.006	0.031

Thermal desorption. The results are illustrated in fig. 3. Ethaline proved slightly better desorption than reline in absolute values, but not statistically significant. The slightly higher absolute desorption values could be related to the higher sorption capacity.

**Figure 3.** Thermal desorption of CO₂ - quantity of gas desorbed from ethaline and reline.

In the case of introduction of CO₂ at 1 atm pressure into the system, the pH decreases from 10.86 to 6.25. After removing CO₂ using inert N₂, the pH returns to its initial value, which means that these DES have reversible acidity/basicity.

The results presented indicate that ethaline could be used for further improvement of CO₂ sorption and desorption by adding amine and /or super-strong basis.

CONCLUSIONS

This study aimed to prepare, characterize and evaluate two deep eutectic solvents, reline and ethaline for CO₂ absorption and desorption, the comparison of desorption capacity for the two DESs being performed for the first time, to the best of our knowledge. The prepared solvents were compared with their commercially available variants in order to have standard references. The four samples (commercial and prepared reline, and commercial and prepared ethaline) were confirmed by FT-IR and characterized for their physical and chemical properties: pH, density, viscosity, refractive index, electrical conductivity.

The values obtained for commercial and prepared solvents are similar. The data are reproducible, confirmable in other specialized works.

Ethaline had 3x better CO₂ absorption (6% versus 2%) and up to 2x better desorption capacity (62.5% versus 34.5%) than reline due to weaker intermolecular interactions, which lead to larger free volume, lower density and viscosity compared to reline.

Normal conditions are not applicable as an "ultra-green" method. Increasing the values of the reaction conditions (temperature and pressure), the absorption capacity of the two eutectics is increased due to physical changes (decreases viscosity and density), allowing easier penetration of the CO₂ molecule into the "eutectic cage". The same applies in the reverse process, desorption. Further studies are necessary to better exploit the DESs potential for CO₂ absorption and desorption.

EXPERIMENTAL SECTION

Materials

Choline chloride was purchased from Sigma-Aldrich, ethylene glycol and urea were purchased from Fluka and used without further purification, but after drying in a vacuum oven. Commercial DES, reline and ethaline, were purchased from Scionix Ltd (U.K.) and used as standard.

Preparation of DES

Choline chloride and urea for reline and choline chloride and ethylene glycol for ethaline were precisely weighed using an analytical balance with 5 decimals [25] [26], thus respecting the molar ratio of 1:2. The preparation took place in a system consisting of a glass round-bottomed vessel, to which a vertical refrigerant was attached (to minimize gas losses in the vessel), an

oil bath (for uniform heating), an electric heating plate with magnetic agitator and a magnetic bar, and a thermometer. The temperature of 40°C was found to be the optimal temperature in order to keep DES liquid at room temperature. The substances were incubated at 600 rpm magnetic stirring for two hours. No release of ammonia from the composition of urea was noticeable. After the reaction was completed, a transparent, colorless, viscous, perfectly homogeneous solution was obtained.

The new eutectic solvents were placed in hermetically sealed plastic containers in desiccators, due to the high hygroscopic character of ChCl. Subsequently, these solvents were characterized for chemical and physical properties and CO₂ absorption and desorption.

DES characterization

The formation of deep eutectic was confirmed by FT-IR and the physico-chemical properties such as pH, density, viscosity, refractive index, and electrical conductivity were determined for the prepared and commercial DESs.

FT-IR. The equipment used was an FT-IR Spectrophotometer - Spectrum GX Perkin Elmer. The FT-IR spectral analysis was performed throughout the wavelength range, from 4000 to 600 cm⁻¹. The samples of ethaline and reline scans were also compared with pure component substances, i.e., choline chloride, ethylene glycol and urea, all three standards being of high analytical purity.

pH. In this study, the pH of the 4 samples was measured using an electrode dedicated to viscous solutions attached to a Mettler Toledo Seven Compact pH meter. Measurements were done at 25°C, with the ATC (automatic temperature correction) function active.

Density. The operating principle of modern appliances is based on the technology of the U(U-tube) glass oscillating tube. A window monitors the existence of gas bubbles which can give measurement errors. The density was determined using a Mettler Toledo EasyD40 densimeter.

Viscosity. Viscosity was determined with a Brookfield DV-II+ Pro viscometer. This parameter is calculated from the resistance encountered by the rotor immersed in the eutectic.

Refractive index. The absolute refractive index is defined as the refractive index of a vacuum medium, which represents the ratio between the speed of light in a vacuum (*c*) and the speed of light in that environment (*v*).

The refractive index of a substance depends on the wavelength of the light. The phenomenon is called the dispersion of light. For transparent and colorless environments, such as the solvents studied, reline and ethaline, the variation of the refractive index in the visible domain is given by Cauchy's relationship:

$$n(\lambda) = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} \quad (3)$$

Different standard refractive indices are used to characterize the dispersion: n_F - the index for the blue line of hydrogen ($\lambda_F = 486.1$ nm); n_D - the index for the yellow line of sodium ($\lambda_D = 589,3$ nm); n_C - the index for the red line of hydrogen (656,3 nm). The refractive index was measured with a Bausch & Lomb Abbe Refractometer.

Electrical conductivity was measured with the conductometer WTW 2FA311 Multi 3320, at room temperature.

CO₂ absorption and desorption

Two experiments were carried out by bubbling a flow of 100% CO₂ (SIAD) in 100 g of DES, at atmospheric pressure with a flow rate of 200 ml/min. Absorption took place in a bubbling vessel fitted with ceramic frieze for better gas dispersion from a supercritical CO₂ equipment – SFT-150-SFE System – Supercritical Fluid Technologies Inc.

The captured CO₂ desorption was performed by two methods, vacuum desorption and thermal desorption. The vacuum desorption took place in a Thermo Scientific Heraeus vacuum oven. Degassing took place at -1bar pressure, 60°C, for 24 hours. The amount of CO₂ desorbed was determined gravimetrically [10]. The thermal desorption system consisted of a thermostatic bath, a round-bottomed balloon, and a magnetic agitator. A fixed amount of solvent was introduced into the flask, the temperature of each sub-experiment was set at 50, 60 or 80°C, at atmospheric pressure, after less than an hour no gravimetrical changes were noticeable).

Free volume calculation

The free volume calculation was performed according to Chhotaray et al. [25], using equations 4 and 5.

$$V_f = V_m - R_r \quad (4)$$

where, V_m is the molar volume (Molar mass/density) and R_m is the molar refraction calculated as follows:

$$R_m = \frac{M}{\rho} \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \quad (5)$$

where M is the molar mass, ρ is the density, and n_D is the refractive index.

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