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Review

Summarizing the Effect of Acidity and Water Content of Deep Eutectic Solvent-like Mixtures—A Review

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Abstract: Deep eutectic solvent-like (DES-like) mixtures re-emerged in green chemistry nineteen years ago and yet have led to a large number of publications covering different research areas and different application industries. DES-like mixtures are considered a special class of green solvents because of their unique properties, such as high solubilization ability, remarkable biocompatibility, low production cost, low volatility, relatively simple synthesis methods, and considerable stability. Several studies have been published that analyze the effect of acidity/alkalinity and water content in DES-like mixtures on their physicochemical properties and behavior. This work summarizes the characterization of green solvents and, subsequently, the influence of various factors on the resulting pH values of green solvent systems. Part of this work describes the influence of water content in DES-like mixtures on their physical and chemical properties. The acidity/alkalinity effect is very important for green solvent applications, and it has the main impact on chemical reactions. As the temperature increases, the pH of DES-like mixtures decreases linearly. The type of hydrogen bond donors has been shown to have an important effect on the acidity of DES-like mixtures. The water content also affects their properties (polarity, solubilization capacity of DES-like mixtures).

Keywords: green solvents; water content; DES-like mixtures; pH; physicochemical properties; acidity

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1. Green Solvent—Deep Eutectic Solvent-like Mixtures

A decisive part of the environmental efficiency of processes in the chemical industry is determined by solvents. These have an impact on process costs, safety, and the health of people. The idea of green solvents expresses the intention to limit the impact on the environment resulting from the use of harmful organic solvents in chemical production. Green solvents must have several different health and safety properties than conventional solvents [1]. In this area of research, ionic liquids (ILs), deep eutectic solvents (DESs), natural deep eutectic solvents (NADESs), and low-transition-temperature solvents or mixtures (LTTMs) are the most used candidates. ILs have been considered green solvents for some time, but they are highly toxic, their preparation is not green, and they are unsatisfactory from the point of view of biological degradability, and therefore they are not in agreement with the basic properties of green solvents [2]. Other disadvantages of ILs include high viscosity, relatively high price, and great effort in their synthesis. Subsequently, due to doubts about the greenness of ILs, a new type of green solvent was discovered—deep eutectic solvents (DESs) [2]. The concept of eutectic mixtures (material which has been a subject in chemistry for literally decades) was applied in 2003 to substances (HBDs and HBAs) that can afford substances whose viscosity is low enough for them to be used as solvents [3].

The application of DESs is a major breakthrough in the field of green chemistry. For conventional organic solvents, DESs appear to be promising substitutes due to their high tunability and preparation using readily available natural compounds. DESs have properties similar to those of ILs, with the advantage of direct and cheap synthesis, which

requires available raw materials from renewable sources [4]. The first definition of DESs was proposed by Abbot et al. [3]. DESs are systems formed from a eutectic mixture of Lewis or Brønsted acids and bases that can contain a variety of anionic and/or cationic species [5] and are ready to combine a suitable hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). Since the definition of DESs requires a melting point close to room temperature, not every combination of HBAs and HBDs will produce DESs [6].

Crystallization of the input compound is prevented by van der Waals interactions and hydrogen bonds, causing the synthesis of mixtures in the liquid state [7–10]. The nature and magnitude of the forces between molecules lead to a wide range of structures [7].

DESs are commonly defined as binary or ternary mixtures of compounds that are joined together through hydrogen bonds. Combining certain compounds in a given molar ratio results in a eutectic mixture. The word "eutectic" means easily "dissolved", and the eutectic point represents the chemical composition and temperature at which a mixture of two solids completely melts at a lower melting point compared to the melting point of either compound [9].

DESs are classified into five categories, where type I consists of a quaternary ammonium salt and a metal halide, and type II mainly includes a quaternary ammonium salt and a hydrated metal halide. Type III represents a mixture composed of a quaternary ammonium salt and various HBDs (carboxylic acids, amides) [10]. Type IV DESs include inorganic transition metals and HBDs, and type V, which is a relatively new class, consists of exclusively non-ionic molecular substances and is normally hydrophobic (Figure 1) [11].

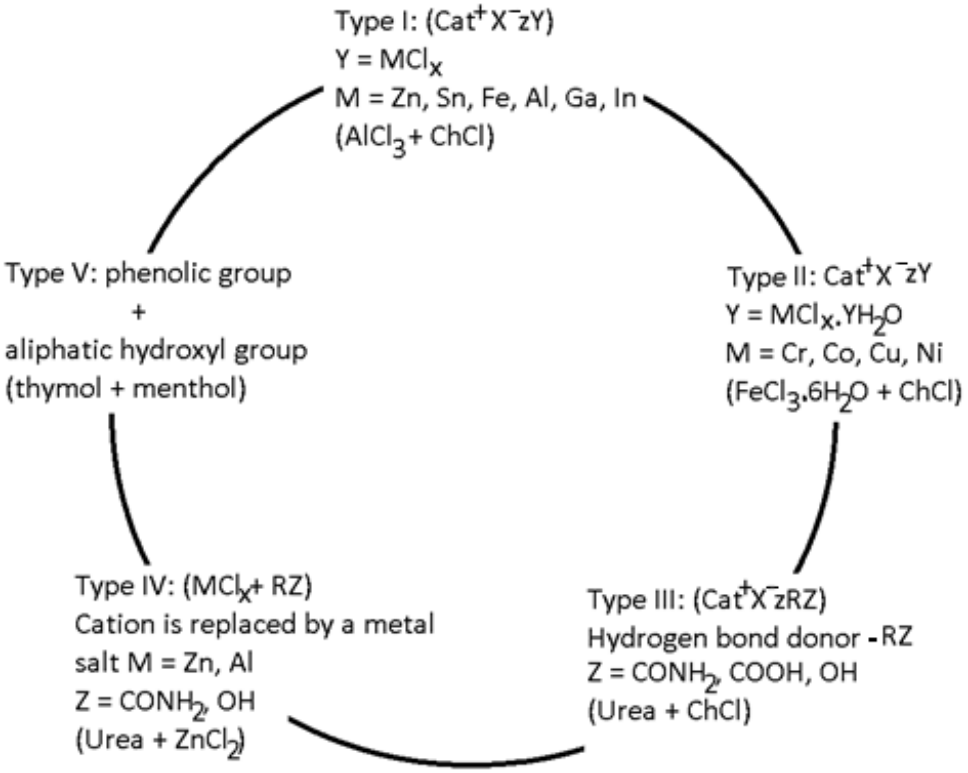

Figure 1. Types of green solvents on the basis of the general formula.

DESs represent eutectic mixtures in the liquid state, which are composed of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). They are synthesized easily and undemandingly by mixing two or three solid components in a certain molar ratio under tolerable conditions (ambient pressure and low temperature). To achieve a liquid state, the mixture of HBA and HBD usually needs to be heated. Hydrogen bonding is responsible for charge delocalization and a melting point that is much lower than that of the individual components. The availability of raw materials, the tunable properties, the

direct and easy synthesis, the biological degradability, and the low toxicity are among the positive properties of DESs [12].

Some living things are capable of producing metabolites (sugars, urea, and organic acids), which when mixed in a certain proportion, form a liquid phase called a natural deep eutectic solvent (NADES). NADESs are considered future solvents and fully recognize the principles of green chemistry [13]. NADESs deserve special attention because of their properties, which make them very promising for future applications. Recently, NADESs have been considered environmentally friendly and green solvents that have attracted much attention from the scientific community. NADESs have various favorable physicochemical properties, such as the liquid state at a wide temperature range, insignificant volatility, chemical and thermal stability, nonflammability, and nontoxicity of the components. In addition, NADES solvents are abundant in nature, easily accessible, and renewable [14]. NADESs are a class of multimolecular solvents formed from a network of hydrogen bonds. They are generally liquids at room temperature that are not very volatile because of their low vapor pressure. Due to their natural origin, they are nontoxic and biocompatible [15]. Most mixtures of these solvents (DESs, NADESs, ILs) show glass transitions instead of melting points, so some solvents have been named low-transition-temperature (LTTM) mixtures. The only common property of these solvents is the mixture of molecules, which leads to a low transition temperature (liquid–solid). Therefore, the term LTTMs appears to be the most representative for the characterization of this large group of solvents [16]. The last period was due to the countless publications on new green solvents (deep eutectic solvents (DESs), natural deep eutectic solvents (NADESs), low melting point mixtures, and low transition temperature mixtures (LTTMs), which basically represent the same group of solvents. In the next sections of this review, we will use the term DES-like mixtures [17] to denote this large group of green solvents. Already in the work of Antenucii et al. [18], DES-like systems were described based on polyols such as HBD and halide salts such as HBA. This term was also used in another work by Ghigo et al. [19], where deep eutectic solvent-like mixtures were created on the basis of glycerol and various organic and inorganic salt halides, which are successfully used as new media in copper-free halodediazonation of arenediazonium salts.

Recently, researchers have revealed potential DES-like mixtures that are suitable for biomass pretreatment; extraction of substances; the pretreatment of cellulose; cellulose modification; and the creation of nanocellulose fibers, nanocrystals, and microcrystalline nanocellulose. The breakdown, fractionation, or/and extraction of lignocellulose biomass (Figure 2) or the modification and treatment of cellulose have been extensively studied in recent decades. The main target is effective pretreatment, which can be achieved via extraction, dissolution of added value substance, and cleavage of lignin structures, the goal of which is to obtain the fibers or substrate without lignin for enzymatic treatment and production of biofuels, or for the production of nanocellulose fibrils, crystals, or modified cellulose. The acidobasic properties of DES-like mixtures have been widely explored because of the need to accurately exploit the data in various industrial and laboratory applications.

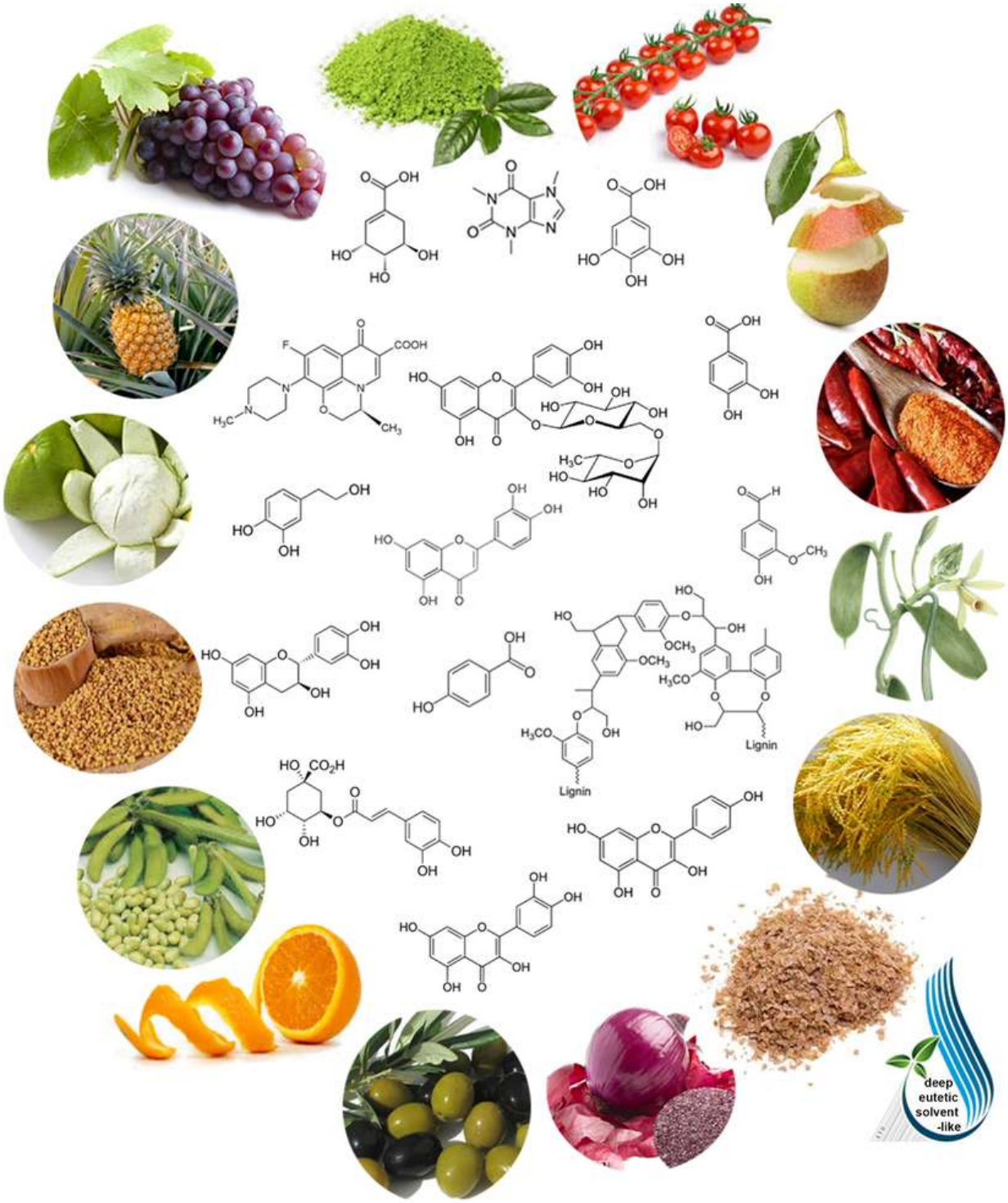

Figure 2. Extraction of lignocelluloses biomass using DES-like mixtures.

2. The Influence of Various Factors on the Resulting Acidity/Alkalinity of DES-like Mixtures

Hydrogen ions (H+) play an important role in all material-related processes, and the pH of solutions is probably the most prominent and widely used chemical concept. The term pH refers to the concentration of hydrogen ions in an aqueous solution, where the term "aqueous solution" means pure water or water with small (in terms of molar amounts) quantities of substances dissolved in it [20]. The concept of pH is very well-defined and is

routinely used in dilute aqueous solutions. The values of pH in different media are related through the Gibbs free energy of the proton exchange between solvents. However, even at the theoretical level, a valid comparability of pH values in different media has been impossible. Since the pH of an aqueous solution is numerically equal to the negative log of the hydrogen ion concentration (in moles per liter), it can be readily calculated using the following equation:

$$\mathrm{pH} = \log\left(\frac{1}{\mathrm{H}^+}\right) \quad (1)$$

It is therefore indicative of the acidic or basic condition of water. However, pH is not equivalent to acidity or alkalinity. Likewise, water having a pH of 9.0 may or may not have more alkalinity than water having a pH of 10.6. Alkalinity and acidity are defined as the ability of an aqueous solution to resist a change in pH. Alkalinity and acidity are measured by determining the amount of a solution of acid or base, as appropriate, of known concentration that is required to completely neutralize the acidity or alkalinity of the aqueous solution [21].

Due to the increased interest in understanding the mechanism of action of eutectic solvents and the demand for natural nontoxic solvents, many articles have been published, and several applications of green solvents have been developed recently. The structural unit of green solvents depends mainly on the interactions between the molecules (between their components). Due to this, basic matrices are affected by temperature, water content, or the proportion of components [15].

Teng et al. [22] prepared binary and ternary DES-like mixtures, which were used for the pretreatment of wheat straw, i.e., to improve the solubility of lignocellulosic material. Choline chloride was chosen as an HBA, and ethanediol and lactic acid were chosen as HBDs (Table 1). The mixture was stirred with a magnetic stirrer and heated to 60 °C (constant temperature) until a clear liquid formed. The prepared DES-like mixtures were placed in a beaker at room temperature. The pH of the prepared DES-like mixtures was analyzed using a pH meter, and the corresponding pH electrode was washed with distilled water and dried. Subsequently, it was placed in a beaker with a DES-like mixture until the indicator was stable. The basicity or acidity of HBD in DES-like mixtures is an important tool in biomass delignification. The pH value of the binary system (choline chloride/urea) was 8.55, which shows weak alkalinity. DES-like mixtures synthesized from choline chloride/lactic acid showed strong acidity because of the presence of lactic acid as an HBD. The ternary DES-like mixtures choline chloride/urea + 10% by weight H_2O and choline chloride/urea + 10% by weight H_2O + 1% by weight NaOH were alkaline, and choline chloride/ethanediol/lactic acid was presented as acidic. Research has revealed that the acidity/alkalinity of DES-like mixtures has a significant effect on the composition of the residue, and that it is necessary to increase the acidity or alkalinity of DES-like mixtures to improve the delignification effect. In contrast, the acidity of DES-like mixtures causes the loss of xylans and part of the cellulose [23].

Table 1. Composition of DES-like mixtures and their pH values (adapted according to Teng et al.) [22].

DES-like Mixtures	Molar Ratio	pH
Choline chloride/Urea	1:2	8.55
Choline chloride/Ethanediol	1:2	3.42
Choline chloride/Lactic acid	1:2	0.25
Choline chloride/Urea + 10 wt% H_2O	1:2	alkaline
Choline chloride/Urea + 10 wt% H_2O + 1 wt% NaOH	1:2	13.41
Choline chloride/Ethanediol/Lactic acid	1:1:1	acidic

Arrora et al. [24] evaluated the valorization of hemicelluloses from lignocellulosic materials (bagasse, rice husk, and wheat straw) to furfural by pH-controlled acid catalysis

using choline-containing DES-like mixtures (Brønsted acid and natural acid DES-like mixtures). In this study, the effect of pH on the catalytic activity of various DES-like mixtures synthesized in a molar ratio of 1:1 was monitored (Table 2). The results showed that choline chloride/p-toluenesulfonic acid (ChCl/p-TSA) is the best at pH 1.0. As the pH increased from 1.0 to 3.0, the furfural yield decreased from 85% to 51%. The molar ratios between HBAs and HBDs were varied from 1:1 to 1:9 to obtain the highest furfural yield with the lowest pH value of DES-like mixtures. The most effective and best results were achieved with choline chloride/p-toluene sulfonic acid and choline chloride/oxalic acid among DES-like Brønsted acid mixtures, and choline chloride/levulinic acid among DES-like mixtures with approximately 85% furfural yield.

Table 2. Valorization of hemicelluloses and furfural yield using different DES-like mixtures * (adapted according to Arrora et al.) [24].

DES-like Mixtures	Molar Ratio	pH	Yield (%)
Choline chloride/p-Toluene sulfonic acid	1:1	1.0	85.4
Choline chloride/Oxalic acid	1:1	1.25	81.6
Choline chloride/Levulinic acid	1:1	1.25	82.0
Choline chloride/Citric acid	1:1	1.34	78.2
Choline chloride/Tartaric acid	1:1	2.2	77.6
Choline chloride/Succinic acid	1:1	2.7	68.0
Choline chloride/Lactic acid	1:1	3.0	51.4

* Conditions of experiments: 100 mg hemicellulose, 5 mmol deep eutectic solvents, 120 °C, 1.5 h.

DES-like mixtures have attracted the attention of researchers because of their environmentally friendly properties and applicability in various applications. Lomba et al. [25] contains information on the toxicity of DES-like mixtures to the environment and the human community. The data obtained were characterized with respect to different factors such as interactions with natural components, pH, organic acid content, or the nature of HBA and HBD. Increased acidity can degrade proteins in membranes and thus cause cell death.

Kareem et al. [26] prepared and analyzed DES-like mixtures composed of phosphonium salts with different HBDs (Tables 3 and 4). The pH of the prepared DES-like mixtures was measured at different temperatures, the change of which was performed using a water bath with temperature control. Physical and chemical properties such as viscosity, pH, density, and conductivity were measured as a function of temperature. The pH behavior was fitted linearly to the general equation:

$$Y = a\ (t/^{\circ}\mathrm{C}) + b \quad (2)$$

where Y is pH, t is the temperature in °C, and a and b are constants (unitless parameters) that vary depending on the type of DES-like mixtures.

The results showed that the nature of the salt, HBD, and the ratio of both compounds have a significant influence on the properties that were analyzed. Furthermore, the type of HBD has been shown to have an important effect on the acidity of DES-like mixtures. The compounds that make up DES-like mixtures, especially HBDs, significantly affect the pH of the final mixture [26]. Furthermore, the authors in [27] presented the idea that a mixture with higher toxicity (higher organic acid content) modifies cell neoplasia and the metabolic pathway. The length of the carbon chain and the presence of certain functional groups (benzene seems to be less toxic than carboxyl or alcohol groups) have an effect on the pH change.

Table 3. Values of constants a and b for Equation (1) (adapted according to Kareem et al.) [26].

DES-like Mixtures	pH	
	a × 10^4	**b**
Methyltriphenylphosphonium bromide/Glycerine	−49	7.0887
Methyltriphenylphosphonium bromide/Ethylene glycol	−89	6.571
Methyltriphenylphosphonium bromide/2,2,2-Triflouracetamide	114	2.4267
Benzyltriphenylphosphonium chloride/Glycerine	22	6.847
Benzyltriphenylphosphonium chloride/Ethylene glycol	−22	5.763

Table 4. Molar ratios, temperature, and pH values of prepared DES-like mixtures (adapted according to Kareem et al.) [26].

DES-like Mixtures	Molar Ratio	Temperature (K)	pH
Methyltriphenylphosphonium bromide/Glycerine	1:1.75	298.15–353.15	~7
Methyltriphenylphosphonium bromide/Ethylene glycol	1:4	298.15–353.15	~6
Methyltriphenylphosphonium bromide/2,2,2-Triflouracetamide	1:8	298.15–353.15	very low, acidic
Benzyltriphenylphosphonium chloride/Glycerine	1:5	298.15–353.15	6.90–7.02
Benzyltriphenylphosphonium chloride/Ethylene glycol	1:3	298.15–353.15	5.71–5.59

DES-like mixtures can be synthesized by a simple and quick mixing of two or more substances in the solid state (one of the two acts as an HBA and the other is an HBD) at a given molar ratio, where the components turn into a liquid by self-association under mild conditions. Natural DES-like mixtures represent a specific class that contains metabolites of vegetable origin in their structure, such as alcohols, sugars, or organic acids. In [28], hydrophobic DES-like mixtures were prepared together with camphor, menthol, and thymol (Table 5). Turmeric (specifically curcumin) was used as biomass to monitor solubility in DES-like mixtures. The solubility of curcumin in different DES-like mixtures was evaluated at room temperature and with mild heating. A pH meter was used to determine the acidity and alkalinity of the DES-like mixture solutions, and these analyses were performed multiple times, and the average values were calculated after the values stabilized. The pH value of the compound/substance is linearly related to the ratio of the hydrogen ion [H+] and hydroxyl ion [OH−] concentrations. The results showed that at a constant concentration of thymol and at an increased concentration of menthol, the pH of DES-like mixtures increased, but no difference in pH was shown when DES-like mixtures were synthesized at room temperature and under mild heating. Similarly, the pH of the DES-like mixtures increased as the camphor concentration was increased. The results of the pH of the DES-like mixtures composed of camphor and menthol showed that when the concentration of menthol increased, the pH also increased, followed by a decrease in the pH of the DES-like mixtures.

Table 5. The pH of hydrophobic DES-like mixtures with and without heat (adapted according to Sekharan et al.) [28].

DES-like Mixtures	Molar Ratio	Conditions	pH
Menthol/Thymol	1:1	10 min, 500 rpm, without heat	6.667 ± 0.037
Menthol/Thymol	1:1	10 min, 30–45 °C, 500 rpm, with slight heat	6.677 ± 0.051
Menthol/Thymol	1:5	48 h, 500 rpm, without heat	6.557 ± 0.037
Menthol/Thymol	1:5	1 h, 30–45 °C, 500 rpm, with slight heat	6.540 ± 0.044
Thymol/Menthol	1:1	10 min, 500 rpm, without heat	6.667 ± 0.037
Thymol/Menthol	1:1	10 min, 30–45 °C, 500 rpm, with slight heat	6.667 ± 0.051
Thymol/Menthol	1:5	48 h, 500 rpm, without heat	6.990 ± 0.037
Thymol/Menthol	1:5	1 h, 30–45 °C, 500 rpm, with slight heat	6.983 ± 0.040
Thymol/Camphor	1:1	10 min, 30–45 °C, 500 rpm, with heat	5.943 ± 0.035
Thymol/Camphor	1:5	1 h, 30–45 °C, 500 rpm, with heat	6.393 ± 0.047
Camphor/Thymol	1:1	10 min, 30–45 °C, 500 rpm, with heat	5.943 ± 0.035
Camphor/Thymol	1:5	1 h, 30–45 °C, 500 rpm, with heat	5.893 ± 0.065
Camphor/Menthol	1:1	10 min, 30–45 °C, 500 rpm, with heat	5.607 ± 0.061
Camphor/Menthol	1:5	1 h, 30–45 °C, 500 rpm, with heat	5.637 ± 0.067
Menthol/Camphor	1:1	10 min, 30–45 °C, 500 rpm, with heat	5.693 ± 0.095
Menthol/Camphor	1:2	30 min, 30–45 °C, 500 rpm, with heat	6.380 ± 0.066

Because of their acceptable properties, the use of DES-like mixtures positively affects the environment because of the usability of available renewable resources. Hayyan et al. [29] in their work analyzed different types of DES-like mixtures containing fructose and choline chloride in different molar ratios (Table 6). Physical properties including pH were measured as a function of temperature over a certain range (25–85 °C). The results showed that decreasing the HBD content resulted in a decrease in pH, but the acidity increased when a higher D-fructose content was used. The pH values decreased with increasing temperature, and all combinations of DES-like mixtures showed a negative effect in reducing pH with increasing temperature in the temperature range of 25 to 85 °C from 6.1 to 4.4 (D-fructose/choline chloride; 1:1), and from 6.8 to 6.3 (D-fructose/choline chloride; 1.5:1). For DES-like mixtures composed of D-fructose and choline chloride in molar ratios of 2:1 and 2.5:1, the pH values ranged from 6.6 to 4.9 and from 7.1 to 6.5, respectively. The pH of all synthesized DES-like mixtures in this publication were more acidic as the temperature increased. As in [19], the relationship between pH and temperature in this study was fitted according to the relationship:

$$\mathrm{pH} = a\,(t/^{\circ}\mathrm{C}) + b \tag{3}$$

where t is the temperature in °C, and a and b are unitless parameters that vary according to the type of DES-like mixtures, and the values of these parameters are listed in Table 6.

Hayyan et al. [30] prepared DES-like mixtures composed of 2-hydroxyethylmethylammonium chloride with D-glucose in different molar ratios of the compounds (1:1; 1.5:1; 2:1; 2.5:1; 1:1.5; 1:2 and 1:2.5). In practice, pH as a physical property of the given systems was measured as a function of temperature (298.15–358.15 K). The pH values of the glucose-based DES-like mixtures ranged from 6.03 to 7.11. When the pH was measured at room temperature, all DESs mixtures showed a neutral pH of around 7. The molar ratio between

the salt (HBA) and the HBD was found to influence the physical properties of the various DES-like mixtures.

Table 6. Values of constants a and b for Equation (2) (adapted according to Hayyan et al.) [29].

DES-like Mixtures	Molar Ratio	pH		Ref.
		a	b/b × 10^5 *	
Choline chloride/D-fructose	1:1	−0.0309	6.9568	[21]
Choline chloride/D-fructose	1.5:1	−0.0100	7.1757	[21]
Choline chloride/D-fructose	2:1	−0.0306	7.5120	[21]
Choline chloride/D-fructose	2.5:1	−0.0116	7.3893	[21]
Choline chloride/D-glucose	1:1	1.671	−1.596 *	[22]
Choline chloride/D-glucose	1.5:1	1.678	−4.554 *	[22]
Choline chloride/D-glucose	2:1	1.692	−8.411 *	[22]
Choline chloride/D-glucose	2.5:1	1.704	−1.309 *	[22]

* parameter b in Equation (2) has the value b × 10^5.

When DES-like mixtures are applied, their nature (acidity and basicity) is important, because these physical properties are among the most important properties that determine their use in various areas of industry. Brønsted acids and bases form the basis of DES-like mixtures. The acidity and basicity of HBD and HBA control the pH of the DES-like mixtures system. Abbott et al. found that the addition of chloride ions to the chloride/glycerol system decreases the acidity of DES-like mixtures and shifts the pH to basic [31]. In addition to the nature of donors and acceptors of hydrogen bonds, pH is also affected by temperature. As the temperature rises, the pH of DES-like mixtures decreases linearly [30].

The subsequent progress in the use of green solvents for additional and untested procedures and processes requires a precise understanding of their properties. The authors in [32] proposed the preparation of three DES-like mixtures based on amines (choline chloride/monoethanolamine, choline chloride/diethanolamine, and choline chloride/methyldiethanolamine) (Table 7). The pH values of the DES-like mixtures were measured at a temperature of 293.15–353.15 K and at three different molar ratios between HBA and HBD (1:6; 1:8, and 1:10). Of the studied DES-like mixtures, DES-like mixtures based on choline chloride/monoethanolamine had the highest pH, and, on the contrary, DES-like mixtures composed of choline chloride/methyldiethanolamine had the lowest pH due to the different chemical structure. The results showed that the pH of the amine-based DES-like mixtures decreased with increasing temperature.

Table 7. pH values of DES-like mixtures depending on the temperature (adapted according to Adeyemi et al.) [32].

DES-like Mixtures	Molar Ratio	Temperature (K)	pH
Choline chloride/Diethanolamine	1:6	295.15–353.15	11.47–9.98
Choline chloride/Methyldiethanolamine	1:6	295.15–353.15	11.04–9.87
Choline chloride/Monoethanolamine	1:6	295.15–353.15	12.81–11.12

Saputra et al. [33] prepared and characterized the thermophysical properties of stable and unknown DES-like mixtures based on ammonium together with HBD and HBA at different molar ratios (Table 8). A correlation (linear regression) was presented between temperature and measured physical properties. The acidity of the ternary DES-like mixtures was measured by immersing the pH meter in the prepared ternary DES-like mixtures

(30–80 °C ± 2 °C). The relationship between temperature and measured pH was correlated using the following equation:

$$\mathrm{pH} = a + b \cdot T \quad (4)$$

where a and b are constants, while T is an arbitrary temperature in °C.

Table 8. Values of constants a and b for Equation (3) (adapted according to Saputra et al.) [33].

DES-like Mixtures	Molar Ratio	pH		
		a	b	R^2
Ethyl ammonium chloride/Glycerol/$ZnCl_2$	1:3:0	2.0816	−0.1336	0.9506
Ethyl ammonium chloride/Glycerol/$ZnCl_2$	1:3:0.25	3.1922	−0.1414	0.9905
Ethyl ammonium chloride/Glycerol/$ZnCl_2$	1:3:0.5	3.5460	−0.1855	0.9749
Ethyl ammonium chloride/Glycerol/$ZnCl_2$	1:4:0	2.4767	−0.1862	0.9411
Ethyl ammonium chloride/Glycerol/$ZnCl_2$	1:4:0.25	3.2751	−0.1350	0.9880
Ethyl ammonium chloride/Glycerol/$ZnCl_2$	1:4:0.5	3.5278	−0.1667	0.9795
Ethyl ammonium chloride/Glycerol/$ZnCl_2$	1:5:0	2.6410	−0.2478	0.9212
Ethyl ammonium chloride/Glycerol/$ZnCl_2$	1:5:0.25	3.1387	−0.1106	0.9854
Ethyl ammonium chloride/Glycerol/$ZnCl_2$	1:5:0.5	3.4876	−0.1491	0.9925

The conclusion is that increasing the temperature achieved a decrease in pH, density, and viscosity and an increase in the electrical conductivity of the synthesized ternary DES-like mixtures. Pure glycerol had the highest pH, which showed that it is a weak acid. When combined with $ZnCl_2$ or ethyl ammonium chloride, the pH value decreased due to the acidic behavior of these compounds. Increasing the molar ratio of HBD ($ZnCl_2$) caused a decreasing trend in the pH of ternary DES-like mixtures (constant molar ratio of glycerol). The formation of hydrogen bonds was inhibited, while molecular vibrations promoted the formation of the [H+] ion, resulting in a decrease in pH [33]. The pH value of DES-like mixtures at different temperatures is shown in Table 9 [34–36]. Generally, it is crucial to estimate the pH of new solvents to understand their dissolution, catalytic and other properties useful for applications [35].

Table 9. pH data of DES-like mixtures at different temperatures (adapted according to Bahadori et al. [34]., Jibril et al. [35], Mjalli et al. [36]).

DES-like Mixtures	Molar Ratio	Temperature (K)	pH	Ref.
Choline chloride/Malonic acid	1:1	298.15	1.67	[34]
Choline chloride/Oxalic acid	1:1	298.15	-	[34]
Choline chloride/Triethanolamine	1:2	298.15	10.66	[34]

Table 9. *Cont.*

DES-like Mixtures	Molar Ratio	Temperature (K)	pH	Ref.
Choline chloride/Zinc nitrate hexahydrate	1:1	298.15	1.00	[34]
Choline chloride/ 2,2,2-Trifluoroacetamide	1:2	298.15	2.36	[34]
N,N-diethylethanol ammonium chloride/Malonic acid	1:1	298.15	0.98	[34]
N,N-diethylethanol ammonium chloride/Zinc nitrate hexahydrate	1:1	298.15	0.52	[34]
Tetrapropylammonium bromide/Ethylene glycol	1:3	293.15–353.15	6.41–5.97	[35]
Tetrapropylammonium bromide/Ethylene glycol	1:4	293.15–353.15	6.53–6.14	[35]
Tetrapropylammonium bromide/Ethylene glycol	1:5	293.15–353.15	7.23–6.57	[35]
Tetrapropylammonium bromide/ Triethylene glycol	1:2.5	293.15–353.15	6.40–6.03	[35]
Tetrapropylammonium bromide/ Triethylene glycol	1:3	293.15–353.15	5.96–5.85	[35]
Tetrapropylammonium bromide/ Triethylene glycol	1:4	293.15–353.15	5.85–5.64	[35]
Tetrapropylammonium bromide/ Glycerol	1:2	293.15–353.15	5.09–4.80	[35]
Tetrapropylammonium bromide/ Glycerol	1:3	293.15–353.15	5.22–4.94	[35]
Tetrapropylammonium bromide/ Glycerol	1:4	293.15–353.15	5.15–4.87	[35]
Tetrabutylammonium chloride/ Glycerol	1:3	293.15–353.15	6.51–6.11	[36]
Tetrabutylammonium chloride/ Glycerol	1:4	293.15–353.15	8.95–7.50	[36]
Tetrabutylammonium chloride/ Glycerol	1:5	293.15–353.15	6.81–6.42	[36]
Tetrabutylammonium chloride/ Ethylene glycol	1:2	293.15–353.15	9.10–7.51	[36]
Tetrabutylammonium chloride/ Ethylene glycol	1:3	293.15–353.15	9.20–7.76	[36]
Tetrabutylammonium chloride/ Ethylene glycol	1:4	293.15–353.15	9.35–8.19	[36]
Tetrabutylammonium chloride/ Triethylene glycol	1:1	293.15–353.15	6.40–5.92	[36]
Tetrabutylammonium chloride/ Triethylene glycol	2:1	293.15–353.15	6.97–6.21	[36]
Tetrabutylammonium chloride/ Triethylene glycol	3:1	293.15–353.15	7.70–6.73	[36]
Tetrabutylammonium chloride/ Triethylene glycol	4:1	293.15–353.15	8.06–7.03	[36]

3. Effect of the Water Content of DES-like Mixtures on Their Physicochemical Properties

Most of the synthesized DESs belong to hydrophilic systems, but some of them have a hydrophobic character, that is, they are immiscible with water. Hydrophobic DESs play an essential role in extracting the dissolved substance in the system and creating a two-phase system. As a result of the polarity of hydrophilic DESs, their applications are limited in terms of nonpolar applications. The chemical structure (nature) of hydrogen bond donors and acceptors has an effect on the hydrophobicity of DESs. Because of the steric hindrance that hinders the charging of the salt with water, the long alkyl chain of the hydrogen bond acceptor leads to the hydrophobicity of DESs, which have low density and moderate viscosity. An increase in the size of the anion leads to an increase in viscosity and a lengthening of the hydrogen bond acceptor chain; in contrast, an increase in temperature decreases the density and viscosity of hydrophobic DES-like mixtures [37].

Most of the DESs appear to be a hygroscopic mixture, so it is difficult to dry this mixture. The addition of water to DESs can cause water to interact with the hydrogen bond donor or acceptor of DESs and subsequently distribute hydrogen bond interactions between the organic salt and the hydrogen bond donor by forming a multi-hydrogen bond, thus reducing the strength of the hydrogen bond [38]. Chen et al. [39] reported that the methyl group had a lower water absorption capacity, and a hydrogen bond donor with a high content of hydroxyl groups had a higher water absorption capacity. Furthermore, the strong interaction between the hydrogen bond acceptor and donor became weaker after the addition of water to the DES system. Furthermore, Kivelä et al. [40] observed that a small amount of water content in DESs affected the physical and chemical properties of the DES by changing the DES from a binary to a ternary system. In addition to the physicochemical properties, the water content in DESs also affects biocompatibility and lowers the melting point, density, and viscosity, because when water is added to the DES system, the hydrogen bonds between the components that make up the DESs are broken. The water content also affects the polarity and solubilization capacity of DESs [41].

The mixing of water and hydrophobic DESs is induced by atmospheric absorption, which causes important effects in this type of solvent. In practice, hydrophobic DESs are ternary mixtures, and this water content causes deviations in the measured values. In [40], the results showed that the density, viscosity, and melting point of DES/water vary linearly with the water content. The conclusion of this work is that a very small addition of water to the hydrophobic DES has an effect mainly on the transport properties. In contrast, the chemical properties of solvents can be disturbed by the presence of water.

Gabriele et al. [42] evaluated the influence of water content in DESs on their properties. DESs were synthesized using choline chloride and glycols. The study of the structure as well as the physicochemical analyses confirmed that without the addition of water to the DES, there are very strong interactions between the acceptor (choline chloride) and hydrogen bond donors (glycols). The addition of water resulted in the weakening of hydrogen bonds, and some properties of DESs were changed; e.g., there was a decrease in viscosity, and an increase in conductivity and polarity. FTIR and NMR spectroscopies showed that upon the addition of water, the H-bonding interactions are weakened by 50% and the DES components are completely dissociated and hydrated at the end.

The authors of [43] developed a green DES-like mixture solvent for the extraction of cannabidiol from industrial hemp leaves. Factors affecting yields were analyzed and investigated in experiments (a factor), namely, the type and concentration of DES-like mixtures, the solid/liquid ratios (hemp/DES-like mixtures), the extraction temperatures and times, and the pH of the DES-like mixture systems (Table 10). Some of these factors were optimized by the response surface method. The Kamlet–Taft polarity parameters were characterized to study the influence of the ability of hydrogen bonds and their polarity on the extractability of DES-like mixtures. Cannabidiol contains two phenolic hydroxyl groups, which means that cannabidiol is a weakly acidic compound. The results showed that the extraction yield increased in the range of pH 1–4 and subsequently decreased with

increasing pH. Under optimized conditions, the highest extraction yield of cannabidiol was 12.22 mg/g. This extraction experiment using DES-like mixtures has advantages in terms of high yields, low costs, easy preparation and handling, and last but not least, environmental friendliness.

Table 10. The pH of the prepared DES-like mixtures was determined at 298 K for all 70 wt% of the aqueous solutions of the DES-like mixtures (adapted according to Cai et al.) [43].

DES-like Mixtures	Molar Ratio	pH
Choline chloride/D-sorbitol	1:1	3.86
Choline chloride/Urea	1:2	8.81
Choline chloride/Oxalic acid	1:1	0.29
Choline chloride/Benzoic acid	1:1	-
Choline chloride/Citric acid	1:1	1.41
Choline chloride/L(+)-Diethyl L-tartrate	1:1	3.38
Choline chloride/Zinc chloride	1:1	4.41
Choline chloride/L(+)-lactic acid	1:1	1.18
Choline chloride/Glycerol	1:2	6.24
Choline chloride/Salicylic acid	1:1	-
Choline chloride/Succinic acid	1:1	1.74
Choline chloride/Mannitol	1:2	-
Choline chloride/Acetamide	1:2	6.38
Betaine/Glycerol	1:2	6.29
Betaine/Citric acid	1:1	2.69
Betaine/Urea	1:2	8.47

Skulcova et al. [44] evaluated the temperature-dependent behavior of 17 DES-like mixtures diluted at pH values of organic acids, amino acids, alcohols, or ammonium salts (Table 11). They studied different types of DES-like mixtures in different molar ratios, which were prepared by mixing at 60–80 °C until homogeneous liquids were formed. The results showed that the pH values continuously decreased with increasing temperature for all DES-like mixtures prepared. DES-like mixtures synthesized from choline chloride/glycerol (1:2) and choline chloride/ethylene glycol (1:2) had the highest pH values of approximately between 4.00 and 4.40. Due to the presence of alcohol and acidic hydrogens in the glycerol and ethylene glycol structures, the pH was lower than 7. In addition, the pH values of the alcohol-based DESs decreased slightly with increasing temperature. Furthermore, it was demonstrated that the presence of acids (HBDs) in DES-like mixtures had a strong influence on the resulting pH, because the pH values of DES-like mixtures containing oxalic and malonic acids decreased sharply with increasing temperature, and thus the nature of the HBD indicated the acidity of the prepared mixture. The conclusion of this study is that the aqueous solutions of the DES-like mixtures showed a pH of 2.74 and below, and except for the two DESs mentioned above, all of the DES-like mixtures prepared and analyzed were acidic, with slightly increasing acidity as the temperature increased. The effect of water was investigated by the NMR technique by comparing the NMR spectra of pure DESs and their mixtures with water in [45,46]. The measured NMR spectra were nearly identical, and it was documented that the presence of water does not break hydrogen bonds in DESs nor violate the eutectic nature of DESs [45,46].

Table 11. Molar ratios, water contents, and pH values of DES-like mixtures used in (adapted according to Skulcova et al.) [44].

DES-like Mixtures	Molar Ratio	Temperature (K)	pH
Choline chloride/Citric acid/H_2O	1:1:1.33	298.15–333.15	1.72–0.92
Choline chloride/Citric acid/H_2O	2:1:1.44	298.15–333.15	1.33–0.98
Choline chloride/Ethylene glycol/H_2O	1:2:0.33	298.15–333.15	4.38–4.00
Choline chloride/Glycerol/H_2O	1:2:0.33	298.15–333.15	4.47–4.12
Choline chloride/Glycolic acid/H_2O	1:3:0.44	298.15–333.15	1.24–0.99
Choline chloride/Lactic acid/H_2O	1:5:0.67	298.15–333.15	1.73–0.99
Choline chloride/Lactic acid/H_2O	1:9:1.11	298.15–333.15	1.61–0.80
Choline chloride/Lactic acid/H_2O	1:10:1.22	298.15–333.15	1.77–1.04
Choline chloride/Malic acid/H_2O	1:1:0.22	298.15–333.15	1.61–0.94
Choline chloride/Malic acid/H_2O	2:1:0.33	298.15–333.15	1.93–1.19
Choline chloride/Malonic acid/H_2O	1:1:0.22	298.15–333.15	1.28–0.41
Choline chloride/Oxalic acid/H_2O	1:1:2.44	298.15–333.15	1.21–0.06
Lactic acid/Alanine/H_2O	9:1:1.11	298.15–333.15	2.15–1.42
Lactic acid/Betaine/H_2O	2:1:0.33	298.15–333.15	2.45–1.85
Lactic acid/Glycine/H_2O	2:1:0.33	298.15–333.15	2.74–2.18
Lactic acid/Glycine/H_2O	9:1:1.11	298.15–333.15	2.27–1.54
Malic acid/Sucrose/H_2O	1:1:0.22	298.15–333.15	2.05–1.35

The behavior of a glass electrode was determined in DESs of different water contents, and it was shown that while the potential–pH plot was Nernstian with high water content, the slope decreased as the amount of water decreased [31]. Mitar et al. [47] noticed that the addition of water to extremely acidic DES increases their pH values, and the addition of water to highly basic DES decreases their pH values. On the other hand, in subsequent work, these authors showed that this conclusion does not hold anymore, as there are difficult-to-predict exemptions to the rule [48].

Knowledge of pH values and pH measurements is very important in various applications (chemical engineering, chemistry). In [49], the authors prepared DES-like mixtures in molar ratios (1:4; 1:10, and 1:16) by mixing allyltriphenylphosphonium bromide salt (HBA) with diethylene glycol and triethylene glycol (HBD) (Table 12). The pH values of the prepared DES-like mixtures were measured in the temperature range of 293.15 to 343.15 K. The conclusions showed that all synthesized DES-like mixtures showed pH values in the acidic range (0.15 to 4.21). As the temperature increased, the pH values of the DES-like mixtures decreased. Furthermore, the results indicated that the molar ratio between salt and HBD had an interesting effect on pH. The pH values increased as more HBD was added to the mixtures. This study shows that not only the temperature and nature of HBD but also the molar ratios between HBA and HBD have an important role in the analysis of pH values.

Table 12. Molar ratios, water contents, and pH values of DES-like mixtures in (adapted according to Ghaedi et al.) [49].

DES-like Mixtures	Molar Ratio	Temperature (K)	pH
Allyltriphenylphosphonium bromide/Diethylene glykol/H_2O	1:4:0.17	293.15–343.15	1.49–0.50
Allyltriphenylphosphonium bromide/Diethylene glycol/H_2O	1:10:0.31	293.15–343.15	4.05–3.23
Allyltriphenylphosphonium bromide/Diethylene glycol/H_2O	1:16:0.39	293.15–343.15	4.21–3.34
Allyltriphenylphosphonium bromide/Triethylene glycol/H_2O	1:4:0.18	293.15–343.15	1.40–0.15
Allyltriphenylphosphonium bromide/Triethylene glycol/H_2O	1:10:0.35	293.15–343.15	3.15–1.90
Allyltriphenylphosphonium bromide/Triethylene glycol/H_2O	1:16:0.56	293.15–343.15	3.42–2.47

Jablonský et al. [50] focused on the synthesis and characterization of the physical and chemical properties of DES-like mixtures containing water. DES-like mixtures were composed of choline chloride along with lactic acid and dihydric alcohols. The pH was analyzed using a digital pH meter at 25 °C, while the concentration of DES-like mixtures was 1 mol/L. The results of the analyzes are shown in Table 13, where it can be seen that the pH values of the prepared DES-like mixtures were in the acidic range.

Table 13. Prepared DES-like mixtures, molar ratios and their pH values at 298.15 K, and the concentration of DES-like mixtures at 1 mol/L (adapted according to Jablonský et al.) [50].

DES-like Mixtures	Molar Ratio	Water Content (%)	pH
Choline chloride/Lactic acid/H_2O	1:2:0.96	5.4	1.71
Choline chloride/Lactic acid/H_2O	1:3:0.97	6.4	1.66
Choline chloride/Lactic acid/H_2O	1:4:0.99	7.1	1.64
Choline chloride/Lactic acid/H_2O	1:5:0.98	7.5	1.63
Choline chloride/Lactic acid/1,3-Propanediol/H_2O	1:1:1:0.92	3.4	1.86
Choline chloride/Lactic acid/1,3-Propanediol/H_2O	1:2:1:0.95	4.8	1.85
Choline chloride/Lactic acid/1,3-Propanediol/H_2O	1:3:1:0.95	5.6	1.80
Choline chloride/Lactic acid/1,3-Propanediol/H_2O	1:4:1:0.92	6.4	1.83
Choline chloride/Lactic acid/1,3-Propanediol/H_2O	1:5:1:0.91	6.8	1.80
Choline chloride/Lactic acid/1,3-Butanediol/H_2O	1:1:1:0.93	2.9	2.05

Table 13. *Cont.*

DES-like Mixtures	Molar Ratio	Water Content (%)	pH
Choline chloride/Lactic acid/1,3-Butanediol/H_2O	1:2:1:0.92	4.5	2.00
Choline chloride/Lactic acid/1,3-Butanediol/H_2O	1:3:1:1	5.4	2.01
Choline chloride/Lactic acid/1,3-Butanediol/H_2O	1:4:1:1	6.1	2.05
Choline chloride/Lactic acid/1,3-Butanediol/H_2O	1:5:1:1	6.4	2.07
Choline chloride/Lactic acid/1,4-Butanediol/H_2O	1:1:1:0.96	3.0	2.31
Choline chloride/Lactic acid/1,4-Butanediol/H_2O	1:2:1:0.92	4.5	2.20
Choline chloride/Lactic acid/1,4-Butanediol/H_2O	1:3:1:0.92	5.5	2.10
Choline chloride/Lactic acid/1,4-Butanediol/H_2O	1:4:1:0.91	6.2	2.10
Choline chloride/Lactic acid/1,4-Butanediol/H_2O	1:5:1:0.91	6.7	2.10
Choline chloride/Lactic acid/1,5-Butanediol/H_2O	1:1:1:0.87	3.9	2.22
Choline chloride/Lactic acid/1,5-Butanediol/H_2O	1:2:1:0.98	5.2	2.18
Choline chloride/Lactic acid/1,5-Butanediol/H_2O	1:3:1:0.90	5.9	2.23
Choline chloride/Lactic acid/1,5-Butanediol/H_2O	1:4:1:0.90	6.7	2.15
Choline chloride/Lactic acid/1,5-Butanediol/H_2O	1:5:1:0.96	6.9	2.13

Panić et al. [48] focused on the development of an easy model to estimate the pH values of DES-like mixtures in a wider range. In this study, the pH of 38 different DES-like mixtures (pH from 0.36 to 9.31) was analyzed, which were subsequently mathematically evaluated using COSMOTherm software and then evaluated using models based on multiple linear regression, linear regression by parts, and artificial neural networks. Analysis of the pH values of DES-like mixtures based on the same HBA and HBD with a change in the water content showed that water had a direct effect on the pH (Table 14) [48]. The estimation of the pH values of DES-like mixtures was based on the quantities R^2, R^2_{adj}, and RMSE-root mean square deviation. Le Mann et al. [51] stated that the model can be considered satisfactory if the coefficient of determination (R^2) is higher than 0.75. The models developed in [48] are applicable to describe the pH values of DES-like mixtures, since the R^2 values for multiple linear regression and piecewise linear regression were 0.7758 and 0.9654, respectively. The results of the RMSE errors show that the multiple linear regression model provides smaller dispersion data (RMSE = 0.6658) compared to the second model (RMSE = 1.865). Based on the results, it can be concluded that the collected findings prove the reliability of the models created in the entire spectrum of the evaluated variables.

Table 14. The pH values of DES-like mixtures measured experimentally (adapted according to Panić et al.) [48].

DES-like Mixtures	Molar Ratio	Water Content (wt%)	pH
Betaine/Citric acid	1:1	30/50	2.46 ± 0.04/2.46 ± 0.02
Betaine/Ethylene glycol	1:2	30	6.86 ± 0.00
Betaine/Glucose	1:1	10	6.64 ± 0.35
Betaine/Glycerol	1:2	30/50	6.77 ± 0.04/6.38 ± 0.07
Betaine/Oxalic acid/ Glycerol	1:2:1	30	2.91 ± 0.05
Betaine/Malic acid	1:1	30/50	2.98 ± 0.01/2.92 ± 0.01
Betaine/Sucrose	4:1	30	7.85 ± 0.11
Choline chloride/Citric acid	2:1	30/50	0.34 ± 0.04/0.71 ± 0.00
Choline chloride/ Ethylene glycol	1:2	10/30	6.19 ± 0.01/6.60 ± 0.57
Choline chloride/ Ethylene glycol	1:2	50/80	4.58 ± 0.14/4.41 ± 0.00
Choline chloride/Fructose	1:1	30/50	3.51 ± 0.05/3.35 ± 0.03
Choline chloride/Glucose	1:1	30/50	4.83 ± 0.06/3.56 ± 0.01
Choline chloride/Glycerol	1:2	30/50	3.71 ± 0.06/2.67 ± 0.11
Choline chloride/Glycerol	1:2	80	3.06 ± 0.01
Choline chloride/Malic acid	1:1	30/50	0.63 ± 0.01/1.03 ± 0.00
Choline chloride/ Proline/Malic acid	1:1:1	10/30	3.23 ± 0.00/2.82 ± 0.01
Choline chloride/ Proline/Malic acid	1:1:1	50	2.63 ± 0.03
Choline chloride/Sorbitol	1:1	50/80	4.92 ± 0.04/3.80 ± 0.08
Choline chloride/Urea	1:2	10/30	9.26 ± 0.08/8.85 ± 0.06
Choline chloride/Urea	1:2	50	8.23 ± 0.04
Choline chloride/ Urea/Ethylene glycol	1:2:2	10	8.29 ± 0.07
Choline chloride/Glycerol	1:2:2	10	8.72 ± 0.05
Choline chloride/Xylose	2:1	30/50	2.86 ± 0.04/3.32 ± 0.03
Choline chloride/Xylose	2:1	80	3.93 ± 0.01
Choline chloride/Xylitol	5:2	30/50	6.90 ± 0.06/6.50 ± 0.01
Choline chloride/Xylitol	5:2	80	6.03 ± 0.06
Choline chloride/Fructose	1:1	30/50	3.51 ± 0.05/3.35 ± 0.03
Citric acid/Glucose	1:1	30	0.53 ± 0.04
Citric acid/Sucrose	1:1	30	0.83 ± 0.00
Fructose/Ethylene glycol	1:2	30	5.31 ± 0.09
Fructose/Glucose/ Ethylene glycol	1:1:2	50	3.67 ± 0.06
Fructose/Glucose/Sucrose	1:1:1	50/80	2.63 ± 0.03/2.99 ± 0.01
Fructose/Glucose/Urea	1:1	30	8.22 ± 0.06
Glucose/Ethylene glycol	1:2	50	4.03 ± 0.02
Glucose/Glycerol	1:2	50	4.33 ± 0.04

Table 14. *Cont.*

DES-like Mixtures	Molar Ratio	Water Content (wt%)	pH
Malic acid/Fructose	1:1	30	0.77 ± 0.01
Malic acid/ Fructose/Glycerol	1:1:1	30	2.77 ± 0.01
Malic acid/Glucose	1:1	30	0.83 ± 0.01
Malic acid/ Glucose/Glycerol	1:1:1	10	0.92 ± 0.00
Malic acid/Sucrose	2:1	30	0.66 ± 0.01
Proline/Malic acid	1:1	10/30	2.63 ± 0.01/2.78 ± 0.02
Proline/Malic acid	1:1	50	2.73 ± 0.03
Sucrose/Ethylene glycol	1:2	30	6.05 ± 0.06
Sucrose/Glucose/Urea	1:1	30	8.14 ± 0.25
Xylose/Ethylene glycol	1:2	30	4.57 ± 0.06

In [52], the physicochemical properties of binary and ternary DES-like mixtures based on choline chloride and lactic acid (binary mixtures) and a combination of choline chloride, lactic acid, and dihydric alcohols (ternary mixtures) were synthesized and characterized. An important feature of DES-like mixtures in terms of their usability in various applications is their acidity, which is indicated by the pH value. The basicity or acidity of DES-like mixtures is mainly influenced by the nature of HBD and temperature. In this work, the pH of diluted solutions of DES-like mixtures was measured using a pH meter at room temperature (approximately 25 °C). The results showed that the pH of the prepared DES-like mixtures was in the acidic range. The pH values for binary mixtures (choline chloride/lactic acid, from 1:1 to 1:5) ranged from 1.71 to 1.63. The pH values for ternary mixtures containing 1,3-butanediol, 1,4-butanediol, or 1,5-pentanediol were always greater than 2.

The water absorption of DES-like mixtures is essential because of their hygroscopic nature and the presence of water at every step. Water is considered an impurity in DES-like mixtures, but some authors in their works deliberately added water to DES-like mixtures in order to improve their performance or fine-tune their properties so that they were usable in desired applications [53–55]. However, on the other hand, the water content in DES-like mixtures has a direct effect on their physicochemical properties and threatens their integrity [56].

4. Pretreatment of Lignocelluloses with DES-like Mixtures

Lignocellulosic biomass is the basic starting material of biorefineries, which leads to the synthesis of biofuels, chemicals, and value-added products. In recent years, a number of articles were published in which the authors focused on the processing of selected types of lignocellulosic biomass using DES-like mixtures. Recent publications have focused on the fractionation of lignocellulosic residues from acacia wood (*Acacia dealbata* Link) [57], pretreatment of corncob [58], and delignification of grass (*Hyparrhenia lipendula*) [59]. Recently, research has also focused on the description of the mechanism of application of DES-like mixtures in the removal of lignin from biomass, while the acidic nature of DES-like mixtures was shown to significantly affect the breaking of mainly labile β–O–4 bonds, and thus the splitting of lignin from biomass. Among the various DES-like mixtures analyzed, acidic DES-like mixtures are popular due to their favorable performance in biomass valorization [60–63]. Another very important area of application of DES-like mixtures is the area focused on the preparation of cellulose nanomaterials (nanofibers, nanocrystals) from biomass and on the modification of cellulose functional groups [64–67]. A notable part of

the biomass is also hemicelluloses, which are the first to degrade from the lignin–saccharide complex as a result of the effect of DES-like mixtures. In the latest published review, Chen et al. [68] summarized the effect of pretreatment with lignocellulosic biomass on the degradation of hemicellulose, while the objective of this review was to point out the need to minimize hemicellulose losses. Among the various DES-like mixtures analyzed, acidic DES-like mixtures showed high efficiency and led to the advancement of their use in biomass pretreatment [69,70]. Acidic DES-like mixtures can be divided into two categories, namely, acidic Brønsted DES-like mixtures and acidic Lewis DES-like mixtures. Both types of acidic DES-like mixtures can facilitate biomass fractionation and support the deconstruction of lignocellulosic materials. Pretreatment with acidic DES-like mixtures selectively solubilizes lignin and hemicellulose while preserving a larger part of cellulose [71]. Considerable efforts are also devoted to the extraction of substances with added value from different types of biomass or waste from biomass processing or animal waste, and more than 1700 articles have been published in recent years, and part of these results have been summarized in an overview of the current state (2020–2022) on the application of various types of DES-like mixtures in the pretreatment of biomass and the separation of these extraction fractions [72–74].

5. Conclusions

Green chemistry and related technologies represent ways of creating and applying products and processes that exclude the synthesis and use of substances that are dangerous to the health of society and the environment. As a result of the increasing demand for green technologies and research concerning them, the development of new, ecological, and green solvents that would meet the requirements and properties of the processes is also progressing. The requirements for green solvents include a reasonable price, low toxicity (nontoxicity for humans and the environment), biodegradability, and the possibility of regeneration. Recently, DES-like mixtures have gained extremely high interest and attention in the scientific and academic community, and publications focused on their characterization and applications have grown exponentially. DES-like mixtures have promising potential for industrial applications as a result of their versatility, simple synthesis, physicochemical properties, and relatively reasonable costs. DES-like mixtures can be mixtures with a large number of structural combinations and physicochemical properties that can be designed and tuned for a real, specific purpose. From the choice of HBD, HBA, and their molar ratio and composition with respect to temperature and water content, DES-like mixtures can be designed and synthesized to meet the requirements of a given process and their application. Among the important properties of DES-like mixtures from the point of view of industrial use (materials of devices and equipment, mass pumping, filtration) are the viscosity, density, and pH values of these solvents. The pH value as such is a very important parameter for all solvents, and in this case, it is one of the critical parameters for the design of DES-like mixtures.

Regarding the efficiency of delignification, the pH of the DES-like mixtures has a significant effect on the final composition of the residue after delignification, whereas the increase in alkalinity and acidity improves the removal of lignin from the biomass, but a low pH value causes the loss of a smaller part of the cellulose and xylan. Changes in the amount of acidity or pH occur depending on the combination of the molar ratio of the mixture and the relative acidity of the cationic and anionic components; that is, the compounds (mainly HBD) and their nature that form DES-like mixtures significantly affect the pH of the final mixture. Changes in pH are also related to the length of the carbon chain and to the presence of some functional groups.

A summary of the results and conclusions of the studies and publications described in this article shows that the type of HBD and salt has a significant effect on the physical behavior of DES-like mixtures. Furthermore, the molar ratio between HBA and HBD was shown to have a decisive influence on the analysis of the physicochemical properties (pH, density, viscosity, and conductivity). In most of the publications in this review, the physical

properties were analyzed as a function of temperature in a certain temperature range. The results show an increase in electrical conductivity and a decrease in pH, density, and dynamic and kinematic viscosity of DES-like mixtures with increasing temperature, and thus the pH of DES-like mixtures tends to become more acidic with increasing temperature.

In addition, the presence of water in DES-like mixtures and its influence on the properties of DES-like mixtures were monitored in this review. It was found that even if the water content is limited to low values, its effects are significant in hydrophobic DES-like mixtures. Furthermore, the existence of water, even in small amounts in DES-like mixtures, affects the physical properties of DES-like mixtures by changing their mixture from binary to ternary. From the point of view of use in various processes and applications, the very low water content in hydrophobic DES-like mixtures has a favorable effect on transport properties. However, on the other hand, water can disrupt the chemical properties of the given solvent.

Several important industrial applications require accurate and clear knowledge of the acidity or alkalinity of a liquid (solvents) defined by the pH value. The physical properties of the studied DES-like mixtures showed that this type of solvent has practical potential use in industry (extraction processes, reactions, and pharmacy). The properties of new and green DES-like mixtures can be predicted at different temperatures for potential applications. The potential of tunable properties makes it possible to use DES-like mixtures as a reaction medium, electrochemical process medium, solvent, or absorbent.

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