

# Physical and Chemical Characterization of Water Containing Choline Chloride-based Solvents with Lactic Acid and Dihydric Alcohol

Michal Jablonsky <sup>1</sup>, Veronika Jancikova <sup>1,\*</sup>, Jozef Sima <sup>2</sup>, Jozef Jablonsky <sup>3</sup>

<sup>1</sup> Institute of Natural and Synthetic Polymers, Department of Wood, Pulp and Paper, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, Bratislava SK-812 37, Slovakia; veronika.jancikova@stuba.sk (V.J.); michal.jablonsky@stuba.sk (M.J.);

<sup>2</sup> Department of Inorganic Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, Bratislava SK-812 37, Slovakia; jozef.sima@stuba.sk (J.S.);

<sup>3</sup> St. Elisabeth University of Health Care and Social Work Bratislava, Nám.1.mája 1, 810 00 Bratislava, Slovakia; jablonskyjozef@gmail.com (J.J.);

\* Correspondence: veronika.jancikova@stuba.sk (V.J.);

Received: 2.02.2022; Accepted: 4.03.2022; Published: 29.03.2022

**Abstract:** This work focused on the preparation, physical and chemical characterization of water containing choline chloride-based solvents with lactic acid and 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, and 1,5-pentanediol, with different molar ratios. Of the physical and chemical properties, we determined density, viscosity, conductivity, and acidity. The results showed that the properties of the resulting solvent could be adjusted by the appropriate selection of another component. It has been shown that the addition of dihydric alcohol can lead to a significant reduction in viscosity and a slight decrease in density, which significantly affects the possibilities of solvent application.

**Keywords:** deep eutectic solvents; physical and chemical characterization; viscosity; density; conductivity; acidity.

© 2022 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Deep eutectic solvents (DESs) have been proposed to replace conventional industrial solvents to decrease environmental pollution and improve the efficiency of the process [1]. DESs have emerged in green chemistry only seventeen years ago and yet resulted in a plethora of publications covering various research areas and diverse fields of application [2]. The low-cost production of DESs production from natural sources and their tunable properties, such as neat null toxicity and biodegradability, make these solvents suitable candidates for various processes within the green chemistry framework [3]. These solvents have significant properties such as cheap ingredients, simple synthesis, easy availability, low vapor pressure, diversity in structures, non-toxic nature, good chemical and thermal stability [4].

DESs are usually comprised of a hydrogen bond acceptor (HBA) compound and a hydrogen bond donor (HBD) compound, which can act as Bronsted–Lewis acids and bases [5]. Commonly, DESs are prepared with bi- or tri- components of hydrogen bond donor and receptor, such as acid amides and quaternary ammonium salts, which usually have a low melting point. DESs are a mixture of HBDs and HBAs with a lower freezing point at room temperature [6, 7].

Despite the fact that the term *deep eutectic solvent* is widespread in describing the green solvents formed by the interaction of a hydrogen bond donor and acceptor, only a small proportion of DESs meets the definition of a eutectic mixture (a homogeneous mixture with single composition and melting temperature corresponding to the eutectic point) [8, 9]. The word *deep* indicates that the melting point of DESs is much lower than that of its pure components. In accordance with the usual practice, the solvents addressed in this contribution will be referred to as DESs. The term low-transition temperature mixtures (LTTMs) is used for both eutectic mixtures (DESs) as well as for liquids composed of natural high-melting-point starting materials which are not eutectic.

DESs/LTTMs are adaptable solvents. This means that their physicochemical properties can be purposefully modified and adjusted to specific requirements within a certain range [10], [11]. The desired properties can be achieved by changing the selection of the individual starting components forming the eutectic mixture and their molar ratio [11]. Other factors that affect the properties of DESs/LTTMs include temperature and water content [11]. Taking into account the practical reasons within the characterization of DESs, attention is paid especially to their viscosity, density, electrical conductivity, acidity/alkalinity, and temperature dependence of the mentioned properties. The findings obtained so far have documented the considerable potential of influencing the properties of DESs/LTTMs by changing the water content, and this aspect is inspected in this paper too. DESs are a new class of green "designer solvent" and their physicochemical properties can be easily tuned by adjusting DES' constituents, chemical ratio, and water content [12].

Regarding the function of water in DES/LTTM, data and opinions published in the literature can be divided into 4 groups:

- water is not considered an integral component of DES/LTTM but only as a solvent of DES/LTTM, e.g., for the purpose of reducing DES/LTTM viscosity [13], [14];

- water is part of the DES/LTTM acting as another component of the DES/LTTM [15];

- water does not affect the properties of the DESs/LTTMs components (results obtained by NMR) [16], [17];

- water affects the properties of DES/LTTM by changing the amount and strength of hydrogen bonds (results obtained by IR and Raman spectroscopy) [18].

This work is a continuation and extension of our paper [19], in which preliminary results on the preparation and properties of some ternary solvents were published. Water is considered to be part of LTTM.

## 2. Materials and Methods

### 2.1. Chemicals.

All reagents, standards, and solvents were of analytical grade. Choline chloride (ChCl) ( $\geq 98.0\%$ ), 1,3-propanediol (98%), 1,3-butanediol ( $\geq 99.5\%$ ), 1,4-butanediol ( $\geq 99.0\%$ ), 1,5-pentanediol ( $\geq 96.0\%$ ) were purchased from Sigma-Aldrich (Germany). Lactic acid (LA) 90.0% solution was obtained from VWR International (USA). Choline chloride was dried under a vacuum. The other chemicals were used as supplied without further treatment.

## 2.2. Preparation of LTTMs.

The LTTMs were prepared by mixing and stirring the corresponding components in a water bath (60 °C; 30 min) to form a homogeneous liquid. The key information about the used LTTMs is summarized in Table 1; their main characteristics are gathered in Table 2.

## 2.3. Apparatus.

The viscoelastic properties were evaluated using a Brookfield DVII + Pro viscometer, as described earlier [13, 14]. The viscosity of samples was measured at different temperatures (20-90 °C) and revolutions (5, 10, 20, and 50 rpm), using a spindle 18 with an adapter. All the measurements were performed 3 times on individual samples. The error of measurement for individual viscosities is in the range of 0.2 to 0.5 mPa·s.

The conductivity measurements were performed in a Conductivity meter, handheld, FiveGo™ F3 equipment. The samples' conductivity was measured at a temperature 298.15 K. All measurements were performed 3 times with individual samples.

The refractive index of the system under investigation was measured using an Abbe refractometer at a temperature of 298.15 K.

The density of the samples was determined using a pycnometer at different temperatures (25 °C–75 °C; (298.15K–348.15 K)). All the measurements were performed 3 times on individual samples.

The pH was determined using a digital pH meter from Hanna Instruments® (Bratislava, Slovakia) at (25 °C; (298.15 K)). The concentration of LTTMs in aqueous solutions was 1 mol/l.

**Table 1.** Prepared LTTMs, and molar ratios of their components.

LTTM No	Component A	Component B	Component C	Component D	Molar ratio	Water content (%)
LTTM1	ChCl	LA	-	Water	1:2:0.96	5.4
LTTM2	ChCl	LA	-	Water	1:3:0.97	6.4
LTTM3	ChCl	LA	-	Water	1:4:0.99	7.1
LTTM4	ChCl	LA	-	Water	1:5:0.98	7.5
LTTM5	ChCl	LA	1,3-propanediol	Water	1:1:1:0.92	3.4
LTTM6	ChCl	LA	1,3-propanediol	Water	1:2:1:0.95	4.8
LTTM7	ChCl	LA	1,3-propanediol	Water	1:3:1:0.91	5.6
LTTM8	ChCl	LA	1,3-propanediol	Water	1:4:1:0.92	6.4
LTTM9	ChCl	LA	1,3-propanediol	Water	1:5:1:0.91	6.8
LTTM10	ChCl	LA	1,3-butanediol	Water	1:1:1:0.93	2.9
LTTM11	ChCl	LA	1,3-butanediol	Water	1:2:1:0.92	4.5
LTTM12	ChCl	LA	1,3-butanediol	Water	1:3:1:1	5.4
LTTM13	ChCl	LA	1,3-butanediol	Water	1:4:1:1	6.1
LTTM14	ChCl	LA	1,3-butanediol	Water	1:5:1:1	6.6
LTTM15	ChCl	LA	1,4-butanediol	Water	1:1:1:0.96	3.0
LTTM16	ChCl	LA	1,4-butanediol	Water	1:2:1:0.92	4.5
LTTM17	ChCl	LA	1,4-butanediol	Water	1:3:1:0.92	5.5
LTTM18	ChCl	LA	1,4-butanediol	Water	1:4:1:0.91	6.2
LTTM19	ChCl	LA	1,4-butanediol	Water	1:5:1:0.91	6.7
LTTM20	ChCl	LA	1,5-pentanediol	Water	1:1:1:0.87	3.9
LTTM21	ChCl	LA	1,5-pentanediol	Water	1:2:1:0.98	5.2
LTTM22	ChCl	LA	1,5-pentanediol	Water	1:3:1:0.90	5.9
LTTM23	ChCl	LA	1,5-pentanediol	Water	1:4:1:0.90	6.7
LTTM24	ChCl	LA	1,5-pentanediol	Water	1:5:1:0.96	6.9

### 3. Results and Discussion

The determined values of refractive index, density, conductivity, and pH are listed in Table 2. Values of conductivity, refractive index, and density were determined as described elsewhere [14, 20].

**Table 2.** Determined properties of LTTMs.

LTTM No	Conductivity (mS/cm)	Refractive index	pH (1 mol/l)	Density (g/cm <sup>3</sup> )					
				25°C	35°C	45°C	55°C	65°C	75°C
LTTM1	1.87	1.4647	1.71	1.197	1.197	1.197	1.197	1.196	1.193
LTTM2	1.84	1.4562	1.66	1.099	1.099	1.099	1.099	1.099	1.099
LTTM3	1.76	1.4523	1.64	1.094	1.094	1.094	1.094	1.094	1.094
LTTM4	1.70	1.4499	1.63	1.070	1.070	1.070	1.070	1.069	1.068
LTTM5	3.45	1.4700	1.86	1.099	1.098	1.098	1.098	1.098	1.098
LTTM6	3.30	1.4614	1.85	1.078	1.078	1.078	1.078	1.078	1.077
LTTM7	2.99	1.4553	1.80	1.076	1.076	1.076	1.076	1.076	1.075
LTTM8	2.60	1.4516	1.83	1.063	1.063	1.063	1.063	1.063	1.062
LTTM9	2.28	1.4488	1.80	1.051	1.051	1.051	1.051	1.051	1.051
LTTM10	2.01	1.4689	2.05	1.083	1.083	1.082	1.082	1.082	1.082
LTTM11	1.95	1.4605	2.00	1.079	1.079	1.079	1.079	1.078	1.077
LTTM12	1.93	1.4547	2.01	1.073	1.073	1.073	1.073	1.073	1.073
LTTM13	1.76	1.4515	2.05	1.037	1.036	1.036	1.036	1.036	1.035
LTTM14	1.59	1.4484	2.07	1.029	1.028	1.028	1.028	1.028	1.027
LTTM15	2.44	1.4703	2.31	1.068	1.068	1.068	1.068	1.068	1.068
LTTM16	2.38	1.4619	2.20	1.067	1.067	1.067	1.067	1.067	1.067
LTTM17	2.27	1.4559	2.10	1.056	1.056	1.056	1.055	1.055	1.055
LTTM18	2.20	1.4527	2.10	1.053	1.053	1.053	1.053	1.053	1.051
LTTM19	2.08	1.4499	2.10	1.017	1.017	1.017	1.017	1.017	1.017
LTTM20	2.24	1.4689	2.22	1.080	1.080	1.080	1.080	1.080	1.079
LTTM21	2.14	1.4541	2.18	1.060	1.060	1.060	1.060	1.059	1.059
LTTM22	2.10	1.4539	2.23	1.058	1.058	1.058	1.058	1.057	1.057
LTTM23	1.96	1.4506	2.15	1.044	1.044	1.044	1.044	1.044	1.043
LTTM24	1.81	1.4500	2.13	1.037	1.037	1.037	1.037	1.037	1.036

#### 3.1. Density.

The densities of individual LTTMs were determined in the temperature range from 25 °C to 75 °C. It can be observed that the individual densities of the ChCl:LA:H<sub>2</sub>O mixtures (LTTM1, LTTM2, LTTM3, LTTM4) change only slightly with the temperature (Table 2). On the other hand, it is evident that the molar ratio of ChCl to LA affects the density of the eutectic mixture ranging from 1.070 g/cm<sup>3</sup> (LTTM4) to 1.197 g/cm<sup>3</sup> (LTTM1) and increasing in the following order: LTTM4 > LTTM3 > LTTM2 > LTTM1 (Table 2). This dependence can be understood as a consequence of the increased molar ratio of organic salt to HBD and/or decreased water content. The first factor may be connected to decreased free volume in the mixtures [21,22].

Table 2 shows the densities of the individual four-component LTTMs, which contained dihydric alcohols in addition to choline chloride, lactic acid, and water (Table 1). In all of them, we can observe the same trend as in the case of binary mixtures. We can also see that the content of organic salt has the same effect on the mixtures as on the three-component ones; their density increases with increasing salt content. However, it should be noted that the addition of dihydric alcohol caused a slight decrease in densities in all ternary mixtures. This observation is in accord with that published by Ondrigova [23]. The highest density (1.099 g/cm<sup>3</sup>) was determined for LTTM5, which is, however, still lower than that of LTTM1 density (1.197 g/cm<sup>3</sup>). By comparing the densities, we found that the carbon chain length of the

dihydric alcohol used also affects the density of solvents. The density of solvents changed with the length of the carbon chain of the dihydric alcohol at room temperature (25 °C). It increased in the following order: 1,4-butanediol > 1,3-butanediol > 1,5-pentanediol > 1,3-propanediol. For ChCl:LA:1,4-butanediol:H<sub>2</sub>O LTTMs, the density ranged from 1.017 to 1.068 g/cm<sup>3</sup>, depending on the composition of the eutectic mixture. For LTTMs consisting of ChCl:LA:1,3-butanediol:H<sub>2</sub>O, the density ranged from 1.028 to 1.082 g/cm<sup>3</sup>, depending on the composition of the eutectic mixture. For LTTMs ChCl:LA:1,5-pentanediol:H<sub>2</sub>O, the density ranged from 1.037 to 1.080 g/cm<sup>3</sup>, depending on the molar ratio of HBA to HBD. As already mentioned, the solvents formed by ChCl:LA:1,3-propanediol:H<sub>2</sub>O in different molar ratios showed the highest density values among all ternary solvents. Their density values ranged from 1.051 to 1.199 g/cm<sup>3</sup>, depending on the ratio of HBA to HBD. It is obvious that there is no linear dependence of the density on the number of carbon atoms in molecules of dihydric alcohols.

The dependence of the densities of LTTMs can be described by the theory of empty vacancies or the theory of hollows [21]. The linear decrease in density with the temperature rise may be due to the faster movement of the molecules and the creation of free space between them [21]. It is also true that with the increasing percentage of water in a given solvent, its density decreases [24]. Density values are also influenced by the molar ratio of organic salt and HBD [21,24]. It is true that with the increasing molar ratio of organic salt to HBD, the structural effect on the liquid increases, and thus the free volume in the liquid decreases [21]. Discussing the density of LTTMs from a practical point of view plays an important role, especially in the delignification process, where it affects the penetration of the solvents into the fiber structure [21,23]. It is clear that the lower density of the solvent, the easier it penetrates the fibers [23]. For the comparison of different molar ratios of ChCl to dicarboxylic acids, the densities decrease with the increase of the molar ratios of ChCl to dicarboxylic acids. This is a result of the much lower densities of ChCl than those of dicarboxylic acids [25,26,29].

### 3.2. Viscosity.

In this work, the viscosity values of individual LTTMs at different temperatures were determined: 20, 30, 40, 50, 60, 70, 80 to 90 °C. The individual dependencies are plotted in the figures below (1 to 5). In Figure 1, we can observe an exponential decrease in the viscosities of binary LTTMs as a function of temperature. LTTM1 at 293.15 K had a viscosity of 255.35 mPa.s, but with a gradual increase in temperature up to 363.15 K, its viscosity decreased to 13.38 mPa.s. For LTTM2, LTTM3, and LTTM4, we observed an identical trend of decreasing viscosities as a function of increasing temperature. We can also observe a decrease in the viscosities of individual binary LTTMs depending on the increasing content of HBD (lactic acid) at a temperature of 293.15 K in the order: LTTM1 (255.35 mPa.s) > LTTM2 (179.4 mPa.s) > LTTM3 (148.7 mPa.s) > LTTM4 (133.45 mPa.s). This trend does not correspond to the statements made in the literature [27] but applies throughout the temperature range. From these dependencies, the same trend can be seen with binary LTTMs - the viscosity value of LTTMs decreases exponentially with increasing temperature. As an example we can mention LTTM5 (ChCl:LA:1,3-propanediol:H<sub>2</sub>O in the ratio 1:1:1:0.92) when the viscosity at 293.15 K is 141.5 mPa.s and at 363.15 K drops to 10.7 mPa.s. An identical trend of decreasing viscosities as a function of increasing temperature can be observed for all ternary mixtures.

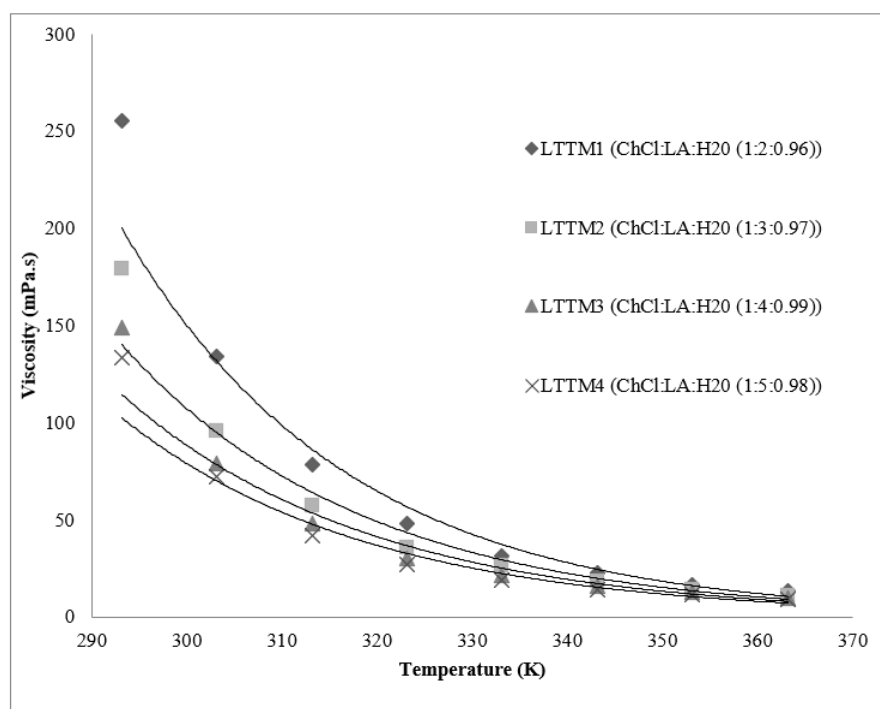
As in the case of binary mixtures, the value of viscosities decreases in the case of ternary mixtures, depending on the increasing content of LA in the solvents. The lowest viscosity among all ternary mixtures was shown by the solvent LTTM19 (ChCl:LA:1,4-butanediol: H<sub>2</sub>O

in the ratio 1:5:1:0.96) 6.7 mPa.s at a temperature of 363.15 K. The lowest viscosity was obtained at the same temperature at binary mixtures, viscosity value only 13.4 mPa.s (LTTM4). Thus, it can be confirmed that the viscosity of LTTMs decreases with the addition of alcohol.

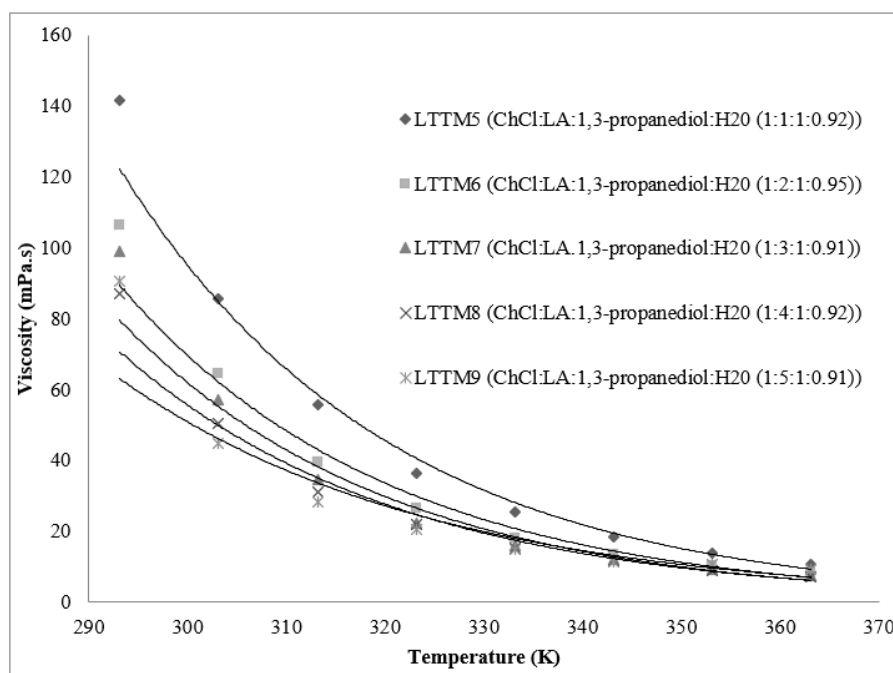
This is in line with the results reported by Ondrigova [23] in her work - the addition of alcohol to a mixture containing ChCl reduces the resulting viscosity of the mixture. It is, therefore, a suitable combination for the preparation of low-viscosity mixtures. Comparing the individual dependences in Figures 1 to 5, we found that the length of the carbon chain of the dihydric alcohol used also affects the resulting viscosity value.

At 293,15 K, the viscosity decreases in the following order depending on the carbon chain length of the alcohol used: 1,3-butanediol (LTTM10 = 214.2 mPa.s, LTTM11 = 156.1 mPa.s, LTTM12 = 127.5 mPa.s, LTTM13 = 120.9 mPa.s, LTTM14 = 132.9 mPa.s) > 1,5-pentanediol (LTTM20 = 194.5 mPa.s, LTTM21 = 141.8 mPa.s, LTTM22 = 114.8 mPa.s, LTTM23 = 108.5 mPa.s, LTTM24 = 95.6 mPa.s) > 1,4-butanediol (LTTM15 = 185.1 mPa.s, LTTM16 = 133.5 mPa.s, LTTM17 = 111.5 mPa.s, LTTM18 = 95.8 mPa.s, LTTM19 = 88.9 mPa.s) > 1,3-propanediol (LTTM5 = 141.45 mPa.s, LTTM6 = 106.5 mPa.s, LTTM7 = 99.1 mPa.s, LTTM8 = 86.9 mPa.s, LTTM9 = 90.5 mPa.s).

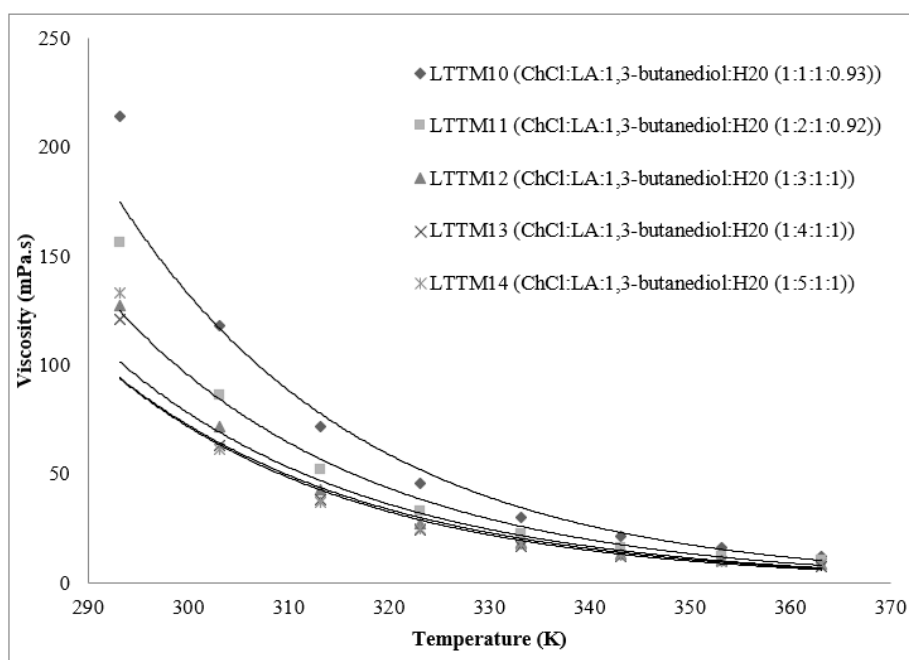
Along with density, viscosity is a key property of LTTMs in terms of their practical use [21]. Most LTTMs show relatively high viscosity values (> 100 mPa.s) at room temperature [28]. High viscosity is always a major barrier to the use of LTTMs for any application but can be significantly reduced by increasing the temperature, increasing the HBA content, or the water content [27]. As the temperature or water content increases, the Van der Waals interactions and hydrogen bonds weaken, decreasing viscosity.



**Figure 1.** Temperature dependence of viscosity investigated LTTMs (LTTM1 to LTTM4).



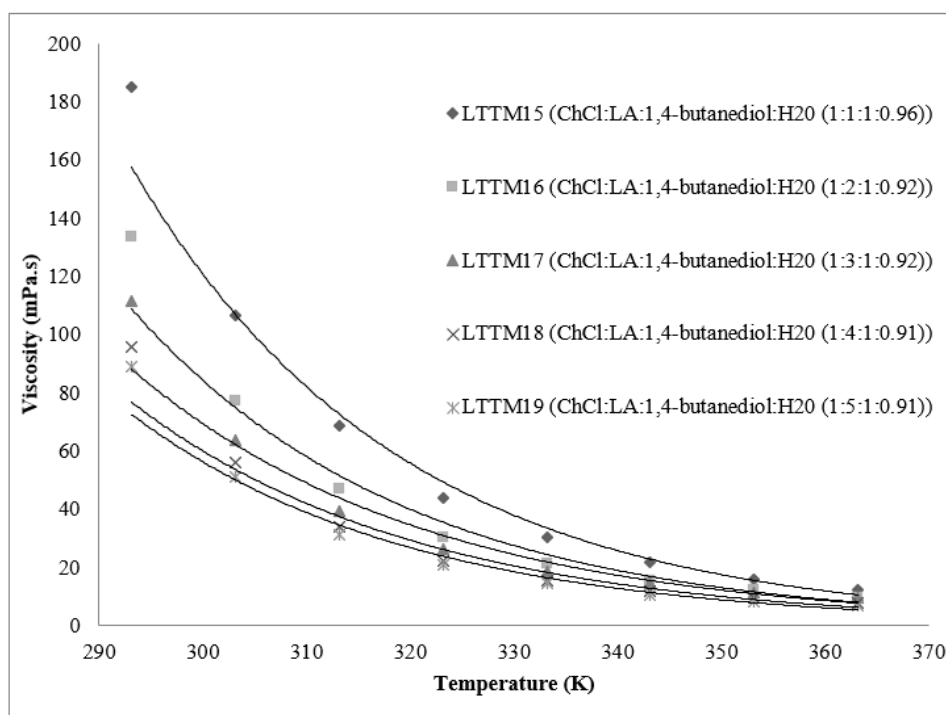
**Figure 2.** Temperature dependence of viscosity investigated LTTMs (LTTM5 to LTTM9).



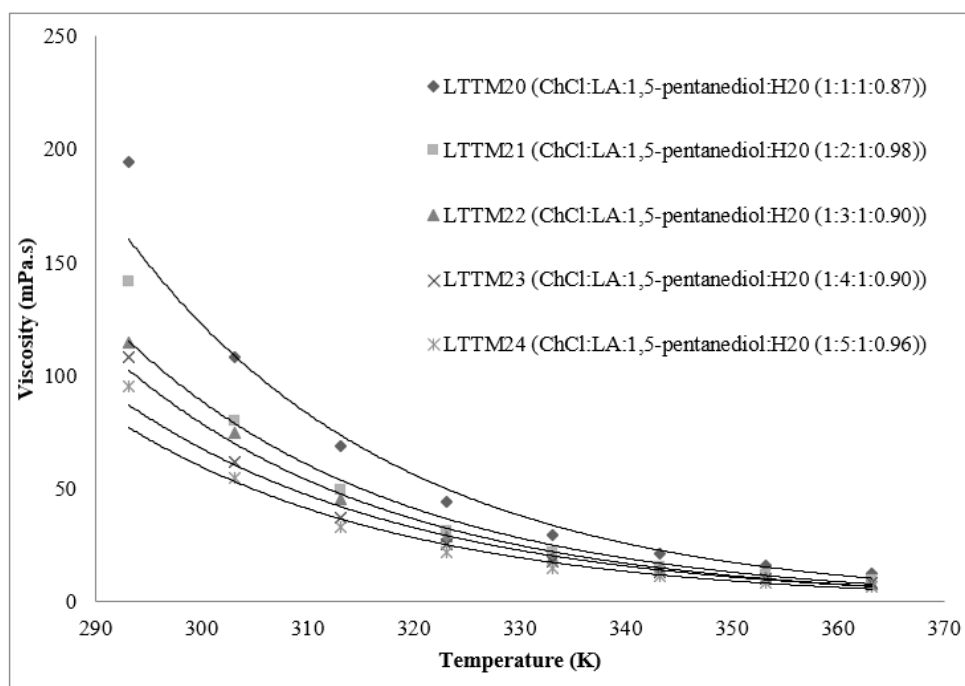
**Figure 3.** Temperature dependence of viscosity investigated LTTMs (LTTM10 to LTTM14).

As already mentioned above, the viscosity of solvents depends on the free volume. Thus the development of new low-viscosity solvents can be described by the so-called theory of holes-free vacancies [21]. The viscosity of LTTMs exhibits Arrhenius behavior - the solvent's viscosity decreases with increasing temperature [21, 28].

Differences in the viscosities are also observed elsewhere for several LTTMs/DESs, and the discrepancies are typically attributed to variable amounts of water contents in the initial samples. Water markedly decreases the viscosity of the LTTMs at lower temperatures because its viscosity is much lower than pseudo-pure LTTMs at temperatures close to ambient conditions [30].



**Figure 4.** Temperature dependence of viscosity investigated LTTMs (LTTM15 to LTTM19).



**Figure 5.** Temperature dependence of viscosity investigated LTTMs (LTTM20 to LTTM24).

### 3.3. Conductivity.

The individual conductivities of binary and ternary LTTMs, which were prepared in different molar ratios (see Table 1), were measured at 25 °C. The results of the measurements are listed in Table 2. The conductivity of the investigated LTTMs decreases with decreasing organic salt content in the solvent, which is consistent with the literature [31]. The highest conductivity value was reached by LTTM5 (3.45 mS/cm), and the lowest conductivity value was shown by LTTM14 (1.59 mS/cm). The results obtained may be applied in the electrochemical industry, where LTTMs act as part of electrolytes [21]. There is a strong correlation between conductivity and viscosity [32]. Most LTTMs show poor ionic



conductivity ( $<2$  mS/cm at room temperature). In general, the conductivities of LTTMs go up with temperature due to a decrease in their viscosity, i.e., their behavior can be described by the Arrhenius equation [32]. Given that changes in the molar ratio of HBA (organic salt) and HBD significantly affect the viscosities of LTTMs, it is clear that they also dramatically affect their conductivity [32]. With increasing organic salt content (e.g., ChCl), the conductivity of the formed mixture increases [31]. In work [33], with the addition of 25 wt% water, conductivities of all LTTMs increase by almost a factor of 2. This behavior is mainly related to the depletion of hydrogen bonds between the components of LTTMs, and the formation of new ones between the water molecules and LTTMs.

#### *3.4. Acidity.*

Another property measured at 25 °C was the pH of the individual LTTMs. The value of pH is important mainly in the fields of biomass delignification and the selection of materials for technological equipment. Delignification in the acidic region is known to have higher delignification efficiency [26]. However, on the other hand, a low initial pH increases the cost of putting this technology into practice due to the high initial investment costs for corrosion-resistant equipment and reactors [26]. The results of measurements are given in Table 2, where we can see that the pH of the individual LTTMs is clearly in the acidic range. The pH of the binary mixtures (LTTM1 to LTTM4) ranged from 1.63 (LTTM4) to 1.71 (LTTM1). The pH value of ternary mixtures containing 1,3-butanediol, 1,4-butanediol, or 1,5-pentanediol always had a  $\text{pH} \geq 2$ . Ternary mixtures containing 1,3-propanediol showed a pH ranging from 1.86 to 1.8. LTTM4, with a pH of 1.63, proved to be the most acidic solvent. The acidity and basicity of the solvents can influence the reaction outcome notably, and hence the precise measurement of pH is important for the reaction [34].

## **4. Conclusions**

The physical and chemical characterization of water containing choline chloride-based LTTMs with lactic acid and 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, and 1,5-pentanediol, with different molar ratios, were measured. It was found that the density and viscosity of the systems decrease with temperature. The addition of dihydric alcohol and the change in the molar ratio of the individual components makes it possible to significantly reduce the viscosities and causes a slight decrease in density, which significantly affects the possibilities of LTTMs application.

## **Funding**

This publication was supported by the Operational Program Integrated Infrastructure for the project: "Strategic research in the field of SMART monitoring, treatment and preventive protection against coronavirus (SARS-CoV-2)," Project no. 313011ASS8, co-financed by the European Regional Development Fund.

## **Acknowledgments**

The authors would like to acknowledge the financial support of the Operation Program Integrated Infrastructure.

## Conflicts of Interest

The authors declare no conflict of interest.

## References

1. Sánchez, P.B.; González, B.; Salgado, J.; Parajó, J.J.; Domínguez, Á. Physical properties of seven deep eutectic solvents based on L-proline or betaine. *The Journal of Chemical Thermodynamics* **2021**, *131*, 517-523, <http://doi.org/10.1016/j.jct.2018.12.017>.
2. Achkar, T.E.; Gerges, H.G.; Fourmentin, S. Basics and properties of deep eutectic solvents – a review. *Environmental Chemistry Letters* **2021**, *19*, 3397-3408, <http://doi.org/10.1007/s10311-021-01225-8>.
3. Antilhan, M.; Aparicio, S. Review and Perspectives for Effective Solutions to Grand Challenges of Energy and Fuels Technologies via Novel Deep Eutectic Solvents. *Energy & Fuels* **2021**, *35*, 6402-6419, <http://doi.org/10.1021/acs.energyfuels.1c00303>.
4. Naseem, Z.; Shehzad, R.A.; Ihsan, A.; Iqbal, J.; Zahid, M.; Pervaiz, A.; Sarwari, G. Theoretical investigation of supramolecular hydrogen-bonded choline chloride-based deep eutectic solvents using density functional theory. *Chemical Physics Letters* **2021**, *769*, 138427, <http://doi.org/10.1016/j.cplett.2021.138427>.
5. Redha, A.A. Review on Extraction of Phenolic Compounds from Natural Sources Using Green Deep Eutectic Solvents. *Journal of Agricultural and Food Chemistry* **2021**, *69*, 878-912, <http://doi.org/10.1021/acs.jafc.0c06641>.
6. Wang, R.; Wang, K.; Zhou, M.; Xu, J.; Jiang, J. Efficient fractionation of moso bamboo by synergistic hydrothermal-deep eutectic solvents pretreatment. *Bioresource Technology* **2021**, *328*, 124873, <https://doi.org/10.1016/j.biortech.2021.124873>.
7. Ji, Q.; Yu, X.; Chen, Li.; Fakayode, O.A.; Zhou C. Synergism of sweeping frequency ultrasound and deep eutectic solvents pretreatment for fractionation of sugarcane bagasse and enhancing enzymatic hydrolysis. *Ultrasonics Sonochemistry* **2021**, *73*, 105470, <http://doi.org/10.1016/j.ultsonch.2021.105470>.
8. Martins, M.A.R.; Pinho, S.P.; Coutinho, J.A.P. Insights into the Nature of Eutectic and Deep Eutectic Mixtures. *Journal of Solution Chemistry* **2019**, *48*, 962-982, <http://doi.org/10.1007/s10953-018-0793-1>.
9. Alhadid, A.; Mokrushina, L.; Minceva, M. Design of Deep Eutectic Systems: A Simple Approach for Preselecting Eutectic Mixture Constituents. *Molecules* **2021**, *25*, 1077, <http://doi.org/10.3390/molecules25051077>.
10. Škulcová, A. Deep eutectic solvents and their use in biomass fractionation. PhD thesis, Slovak Technical University in Bratislava, Bratislava, **2018**.
11. Yang, Z. Natural deep eutectic solvents and their applications in biotechnology. *Applications of Ionic Liquids in Biotechnology* **2018**, *168*, 31-59, [http://doi.org/10.1007/10\\_2018\\_67](http://doi.org/10.1007/10_2018_67).
12. Zhang, K.; Wang, Y.; Li, S.; Zhu, G. Air-assisted liquid-liquid microextraction based on the solidification of floating deep eutectic solvents for the simultaneous determination of bisphenols and polycyclic aromatic hydrocarbons in tea infusions via HPLC. *Food Chemistry* **2021**, *348*, 129106, <http://doi.org/10.1016/j.foodchem.2021.129106>.
13. Škulcová, A.; Russ, A.; Jablonský, M.; Šima, J. The pH behavior of seventeen deep eutectic solvents. *Bioresources* **2018**, *13*, 5042-5051, <http://doi.org/10.15376/biores.13.3.5042-5051>.
14. Jablonský, M.; Škulcová, A.; Ház, A.; Majová, V.; Šima, J. Long-term Isothermal stability of Deep Eutectic Solvents. *Bioresources* **2018**, *13*, 7545-7559, <http://doi.org/10.15376/biores.13.4.7545-7559>.
15. Jablonský, M.; Šima, J. Phytomass Valorisation by Deep Eutectic Solvents – Achievements, Perspectives and Limitations. *Crystals* **2021**, *10*, 800, <http://doi.org/10.3390/cryst10090800>.
16. Delso, I.; Lafuente, C.; Muñoz-Embid, J.; Artal, M. NMR study of choline chloride-based deep eutectic solvents. *Journal of Molecular Liquids* **2019**, *290*, 111236, <http://doi.org/10.1016/j.molliq.2019.111236>.
17. Zhekenov, T.; Toksanbayev, N.; Kazakbayeva, Z.; Shah, D.; Mjalli, F.S. Formation of type III deep eutectic solvents and effect of water on their intermolecular interactions. *Fluid Phase Equilibria* **2017**, *441*, 43-48, <http://doi.org/10.1016/j.fluid.2017.01.022>.
18. Ahmadi, R.; Hemmateenejad, B.; Safavi, A.; Shojaeifard, Z.; Shahsavari, A.; Mohajeri, A.; Zolghadr, A.R.; Heydari-Dokoohaki, M. Deep Eutectic-Water Binary Solvent Associations Investigated by Vibrational Spectroscopy and Chemometrics. *Physical Chemistry Chemical Physics* **2018**, *20*, 18436, <http://doi.org/10.1039/c8cp00409a>.

19. Jablonský, M.; Majová, V.; Stržincová, P.; Šima, J.; Jablonský, J. Investigation of Total Phenolic Content and Antioxidant Activities of Spruce Bark Extracts Isolated by Deep Eutectic Solvents. *Crystals* **2020**, *10*, 402, <http://doi.org/10.3390/cryst10050402>.
20. Hayyan, A.; Mjalli, F.S.; AlNashef, I.M.; Wahaibi, T.A.; Wahaibi, Y.M.A.; Hashim, M.A. Fruit sugar-based deep eutectic solvents and their physical properties. *Thermochimica Acta* **2012**, *541*, 70-75, <http://doi.org/10.1016/j.tca.2012.04.030>.
21. Škulcová, A. Deep eutectic solvents and their use in biomass fractionation. PhD thesis, Slovak Technical University in Bratislava, Bratislava **2018**.
22. Davis, S. J. Deep eutectic solvents derived from inorganic salts. Thesis submitted for the degree of Doctor of Philosophy at the University of Leicester **2015**.
23. Ondrigová, K. Delignification of pulps with deep eutectic solvents. Diploma thesis, Slovak Technical University in Bratislava, Bratislava **2018**.
24. Fischer, V. Properties and Applications of Deep Eutectic Solvents and Low-Melting Mixtures. PhD thesis, Fakultät für Chemie und Pharmazie der Universität Regensburg **2015**.
25. Li, C.; Cai, Z.; Ma, Y.; Cao, Y.; Huang, K.; Jiang, L. Densities and viscosities of, and solubilities of acidic gases (SO<sub>2</sub> and H<sub>2</sub>S) in natural deep eutectic solvents. *The Journal of Chemical Thermodynamics* **2022**, *167*, 106713, <http://doi.org/10.1016/j.jct.2021.106713>.
26. Jablonský, M.; Majová, V.; Ondrigová, K.; Šima, J. Preparation and characterization of physicochemical properties and application of novel ternary deep eutectic solvents. *Cellulose* **2015**, *5*, 3031-3045, <http://doi.org/10.1007/s10570-019-02322-2>.
27. Zhao, B.Y.; Xu, P.; Yang, F.X.; Wu, H.; Zong, M.H.; Lou, W.Y. Biocompatible Deep Eutectic Solvents Based on Choline Chloride: Characterization and Application to the Extraction of Rutin from *Sophora japonica*. *ACS Sustainable Chemistry & Engineering* **2015**, *3*, 2746-2755, <http://doi.org/10.1021/acssuschemeng.5b00619>.
28. Hizaddin, H.F.B. Selection of ionic liquids and deep eutectic solvents via quantum chemical methods and liquid-liquid equilibria involved in the extractive denitrogenation of diesel. PhD thesis, University of Malaya, Kuala Lumpur, Malaysia **2016**, <http://studentsrepo.um.edu.my/id/eprint/6670>.
29. Klapp, E.C.; Parra, N.G.; Aravena, P.; Lama, H.Q.; Held, C.; Canales, R.I.; Garrido, J.M. Interfacial Properties of Deep Eutectic Solvents by Density Gradient Theory. *Industrial & Engineering Chemistry Research* **2022**, <http://doi.org/10.1021/acs.iecr.1c03817>.
30. Parra, N.F.G.; Figueroa, V.P.C.; Aravena, P.; Vesovic, V.; Canales, R.I. Viscosity of Choline Chloride-Based Deep Eutectic Solvents: Experiments and Modeling. *Journal of Chemical & Engineering Data* **2021**, *65*, 5581-5592, <http://doi.org/10.1021/acs.jced.0c00715>.
31. Abbott, A.; Capper, G.; Boothby, D.; Davies, D.L.; Rasheed, R.K. Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. *Journal of the American Chemical Society* **2004**, *29*, 9142-7, <http://doi.org/10.1021/ja048266j>.
32. Zhang, Q.; Vigier, K.D.O.; Royer, S.; Jérôme, F. Deep eutectic solvents: syntheses, properties and applications. *Chemical Society Reviews* **2012**, *41*, 7108-7146, <http://doi.org/10.1039/c2cs35178a>.
33. Celebi, A.T.; Vlugt, T.J.H.; Moulton, O.A. Thermal conductivity of aqueous solutions of reline, ethaline, and glyceline deep eutectic solvents; a molecular dynamics simulation study. *Molecular Physics* **2021**, *119*, <http://doi.org/10.1080/00268976.2021.1876263>.
34. Li, M.; Zhu, C.; Fu, T.; Gao, X.; Ma, Y. Effect of water on amine-based deep eutectic solvents (choline chloride + monoethanolamine): Structure and physicochemical properties. *Journal of Environmental Chemical Engineering* **2022**, *10*, 106592, <http://doi.org/10.1016/j.jece.2021.106592>.