

*J. Serb. Chem. Soc.* 82 (9) 1039–1052 (2017)  
JSCS–5021

Journal of  
the Serbian  
Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

UDC 541.12.017:547.421–327:544.35:  
544.2.004.12

*Original scientific paper*

## The physicochemical and thermodynamic properties of the choline chloride-based deep eutectic solvents

DRAGAN Z. TROTER<sup>1</sup>, ZORAN B. TODOROVIĆ<sup>1</sup>, DUŠICA R. ĐOKIĆ-STOJANOVIĆ<sup>2</sup>,  
BILJANA S. ĐORDEVIĆ<sup>1</sup>, VANJA M. TODOROVIĆ<sup>3</sup>, SANDRA S. KONSTANTINOVIC<sup>1</sup>  
and VLADA B. VELJKOVIĆ<sup>1\*</sup>

<sup>1</sup>Faculty of Technology, University of Niš, Bulevar Oslobođenja 124, 16000 Leskovac, Serbia,

<sup>2</sup>Zdravlje Actavis, Vlajkova 199, 16000 Leskovac, Serbia and <sup>3</sup>Faculty of Pharmacy,  
University of Belgrade, Vojvode Stepe 450, 11221 Belgrade, Serbia

(Received 25 February, revised 22 May, accepted 23 May 2017)

**Abstract:** This paper reports the physicochemical (density, dynamic viscosity, electrical conductivity and refractive index) and the thermodynamic (thermal expansion coefficient, molecular volume, lattice energy and heat capacity) properties of several choline chloride (ChCl) based deep eutectic solvents (DESs), with 1:2 mole ratio, respectively: ChCl:propylene glycol, ChCl:1,3-dimethylurea and ChCl:thiourea, at atmospheric pressure as a function of temperature over the range of 293.15–363.15 K. Their properties were also compared with those of some already characterized ChCl-based DESs, namely ChCl:ethylene glycol, ChCl:glycerol and ChCl:urea (1:2 mole ratio). Density, viscosity and refractive index of all DESs decrease with the increasing temperature while the electrical conductivity increases. Viscosity and conductivity of the tested DESs were fitted by both Arrhenius-type and Vogel–Tamman–Fulcher equations. The changes of molar enthalpy, entropy and Gibbs energy of activation, determined using the Eyring theory, demonstrated the interactional factor as predominant over the structural factor for all DES systems. The fractional Walden rule, used to correlate molar conductivity and viscosity, showed an excellent linear behaviour. It was shown that ChCl:propylene glycol DES had properties similar to ChCl:ethylene glycol and ChCl:glycerol DESs. However, the properties (density, viscosity and electrical conductivity) of ChCl:1,3-dimethylurea and ChCl: thiourea DESs were inferior to those of the ChCl:urea DES.

**Keywords:** physicochemical properties; eutectic; glycols; amides.

### INTRODUCTION

Having highly low volatility and being less toxic, ionic liquids (ILs) are very convenient to replace organic solvents. Containing only ions, ILs can easily be

\* Corresponding author. E-mail: veljkovicvb@yahoo.com  
<https://doi.org/10.2298/JSC170225065T>

designed to be in the liquid state at or even below room temperature by choosing adequate starting chemicals.<sup>1</sup> Their favorable properties make ILs environmentally acceptable.<sup>2,3</sup> Many ILs applications have been described, such as in electrochemistry and extraction<sup>4</sup>, catalysis and enzyme-catalyzed reactions.<sup>5</sup> However, since some ILs are still toxic,<sup>6,7</sup> their use in drug- and food-related products is unacceptable. Deep eutectic solvents (DESs) have been referred as promising alternative to the conventional ILs. In comparison with ILs, DESs are cheaper, easier for preparation and biodegradable,<sup>8-10</sup> referring them as green solvents. DESs are usually made by combining a substituted quaternary ammonium salt and a complexing agent (usually a hydrogen bond donor, HBD), resulting in the compound with lower melting point.<sup>5,8,11</sup> Designing new green solvents requires using safe and environmentally friendly compounds. The most used substituted quaternary ammonium salt is choline chloride (2-hydroxy-ethyltrimethyl-ammonium chloride, ChCl), which is an essential micronutrient and human nutrient,<sup>12</sup> used as an additive in animal feeds. As HBDs, polyols are often used, and among them, glycerol and ethylene glycol are the most dominant. Glycerol has a lot of advantages, such as being non-toxic, biodegradable and recyclable, and is produced on a large scale from renewable sources.<sup>13</sup> On the other hand, ethylene glycol, although used in various industrial applications, is moderately toxic liquid. Safer option is propylene glycol, a non-toxic polyol used in food processing, as a solvent in many pharmaceutical formulations, and for the production of polymers. It is also one of the major ingredients (together with glycerol) of the so-called “e-liquids” used for electronic cigarettes. Besides polyols, urea and its derivatives can also be chosen as safe HBDs. Urea is mostly used as a nitrogen-release fertilizer, while 1,3-dimethylurea and thiourea have been used in different chemical syntheses.

For the general understanding, the optimization of the performance and the increase of the potential future application of DESs, it is important to know or be able to predict their thermodynamic and physicochemical properties. Therefore, further investigations of the most important properties of DESs, such as density, viscosity, heat capacity, electrical conductivity or refractive index, are needed for expanding their use. Both physicochemical and thermodynamic properties of DESs must be known for their uses in different industrial and laboratory processes. Knowing the density ( $\rho$ ) of the DESs is very important for many different industries, because the density measurement helps to determine the characteristics of the DESs. Besides being measured in a laboratory, the density data of different DESs were also predicted by different ways, such as by Rackett models,<sup>14</sup> the parachor parameter and surface tension data,<sup>15</sup> as well as the Lorentz–Lorentz equation.<sup>16</sup> Mjalli *et al.* modified the Rackett model<sup>17</sup> and recently Mjalli used the molecular structure explained by the mass connectivity index for predicting the density of the DESs.<sup>18</sup> Dynamic viscosity ( $\eta$ ) is a very important

transport property, especially for equipment design and fluid flow calculations. Viscosity data of DESs are useful in selecting the optimum salt:HBD ratio, which results in saving material and energy for the preparation of DESs. Knowing the electrical conductivity ( $\kappa$ ) of a DES is of great value, if it is used as a supporting electrolyte in electrochemical experiments. The higher is the electrical conductivity exhibited, the lower is the ohmic drop during electrolysis and the cell voltage, resulting in higher energy efficiency. The refractive index ( $n_D$ ) has a unique value for every material and has a very important role in material engineering. Unlike other properties, the measurements of refractive index of DESs are rarely done, so there is a lack of such data in the literature. Once physical properties of DESs have been fully characterized, they can be used to calculate thermodynamic properties of DESs' systems (such as entropy, enthalpy, *etc.*). Since these properties establish the criteria for the determination of the feasibility or spontaneity of a given transformation, the energy exchanges that occur in the DESs' systems can be predicted, which is crucial for the chemical industry.

The present paper focuses onto the ChCl-based DESs with different HBDs (propylene glycol, ethylene glycol, glycerol, urea and 1,3-dimethylurea and thiourea) prepared in the mole composition of 1:2. It is worth to emphasize, as far as the authors are familiar with, most physicochemical and thermodynamic properties of the ChCl:propylene glycol, ChCl:1,3-dimethylurea and ChCl:thiourea DESs have not been studied yet. Both physical (density, dynamic viscosity, electrical conductivity and refractive index) and thermodynamic (thermal expansion coefficient, molecular volume, lattice energy and heat capacity) properties were studied at the atmospheric pressure in the temperature range of 293.15–363.15 K. While density and viscosity of ChCl:ethylene glycol, ChCl:glycerol and ChCl:urea have already been investigated,<sup>14,19–24</sup> the data on their other properties are very scarce.<sup>19,22–24</sup> The Arrhenius exponential type dependence and Vogel–Tamman–Fulcher equation were employed for the understanding of the transport properties of the studied DESs. The thermodynamic characteristics of viscous flow were also determined. In addition, the fractional Walden rule was employed for describing the relationship between molar conductivity and viscosity for the DESs.

## EXPERIMENTAL

### *Chemicals*

ChCl, ethylene glycol and 1,3-dimethylurea (all  $\geq 98.0\%$ ) were obtained from Sigma Aldrich (St. Louis, USA), while propylene glycol and glycerol (both Ph Eur grade) were purchased from MeiLab (Belgrade, Serbia). Urea and thiourea (both 99.5%) were obtained from Zorka (Šabac, Serbia). All chemicals were used as purchased, without any purification.

### *Preparation of DESs*

ChCl was combined with the selected HBD, namely propylene glycol, ethylene glycol, glycerol, urea, 1,3-dimethylurea and thiourea, at the 1:2 mole ratio in a round-bottomed flask placed on a rotary evaporator and held at 348.15 K within 2 h (until the homogeneous, trans-

parent liquid was formed). The DESs were stored in the well-closed glass bottles in a desiccator containing  $\text{CaCl}_2$ . All DESs are viscous, homogeneous and colorless liquids. However, ChCl:urea DES turns into white semi-solid with time, while ChCl:1,3-dimethylurea and ChCl:thiourea DESs turn into white solid upon cooling. The water content of the dried DESs, determined by the Karl-Fischer method (Metrohm 73KF coulometer) were less than 350 ppm. Fig. S-1 of the Supplementary material to this paper shows the preparation of the ChCl-based DESs schematically and FTIR spectra of the DESs and their components are presented in Fig. S-2 of the Supplementary material.

#### *Physicochemical properties of DESs*

All physicochemical properties were measured in the temperature range between 293.15 and 363.15 K at the atmospheric pressure. The readings were taken after 20 min at each temperature to provide a good temperature equilibration. Density, dynamic viscosity and electrical conductivity were measured using a DMA 4500 Anton Paar densitometer, a rotational viscometer (Visco Basic Plus, ver. 0.8, Fungilab S.A., Barcelona, Spain) and a ProLine conductivity meter B250, respectively. Refractive index values were obtained by an automatic Atago refractometer A100. All measurements were performed in triplicates.

### RESULTS AND DISCUSSIONS

#### *Effect of temperature on density of the ChCl-based DESs*

Fig. 1 shows the dependence of the density of the studied DESs on temperature.

The present results showed that the density decreases with the increase of the temperature, as usual for liquids. For the purpose of comparison, the literature data for the ChCl:ethylene glycol, ChCl:glycerol and ChCl:urea systems are also presented. As in the case of pure ILs,<sup>25,26</sup> as well as ChCl:ethylene glycol, ChCl:glycerol and ChCl:urea,<sup>27-29</sup> a very good linear correlation (see Supplementary material) between density and temperature was observed for all DESs systems studied.

Based on the coefficient of volume expansion, among DESs with polyols, ChCl:glycerol is the most thermally sensitive, followed by ChCl:ethylene glycol and ChCl:propylene glycol, while among DESs with amides, the most thermally sensitive is ChCl:1,3-dimethylurea, then ChCl:thiourea and lastly ChCl:urea.

At the room temperature, the density of the tested DESs is in the following order: ChCl:glycerol > ChCl:propylene glycol > ChCl:urea > ChCl:ethylene glycol while ChCl:1,3-dimethylurea and ChCl:thiourea are solid and become liquid after heating. At 313.15 K, the densities of the tested DESs follow the order: ChCl:1,3-dimethylurea > ChCl:thiourea > ChCl:propylene glycol > ChCl:glycerol > ChCl:urea > ChCl:ethylene glycol. The difference in density can be explained by the different molecular arrangement, or packing of the DES. ChCl:propylene glycol DES has a higher density than other two polyol-based DESs because of the higher intermolecular packing of the compound structure. The density of ChCl:ethylene is lower than those of other polyol-based counterparts, showing that higher-density liquids have a more compact structure. In the case of

ChCl:1,3-dimethylurea and ChCl:urea, the electron rich oxygen part easily interacts with ChCl, but ChCl:1,3-dimethylurea is denser, which can be attributed to the tight intermolecular packing between ChCl and HBD. The presence of two methyl groups in this DES influences its density greatly, since it is higher than the density of ChCl:thiourea.

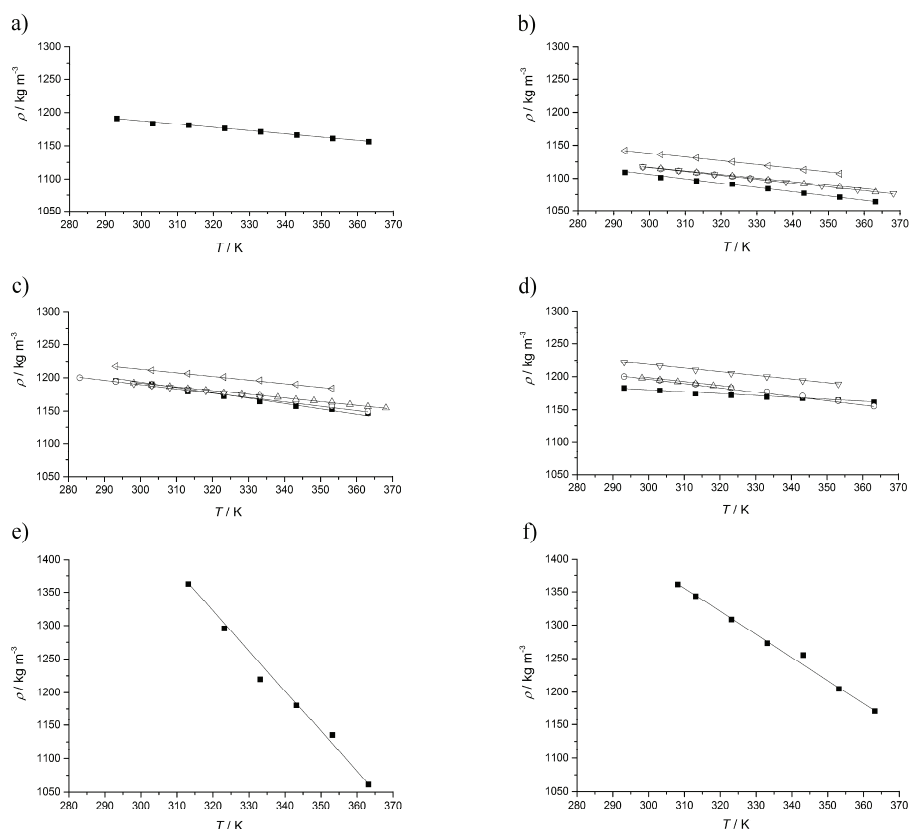


Fig. 1. Temperature dependence of the density of the studied eutectic mixtures: a) ChCl:propylene glycol – ■ (our values); b) ChCl:ethylene glycol – ■ (our values),  $\nabla$ <sup>14</sup>,  $\circ$ <sup>19</sup>,  $\triangle$ <sup>20</sup> and  $\triangleleft$ <sup>21</sup>; c) ChCl:glycerol – ■ (our values),  $\nabla$ <sup>19</sup>,  $\triangle$ <sup>20</sup>,  $\triangleleft$ <sup>21</sup> and  $\circ$ <sup>22</sup>; d) ChCl:urea – ■ (our values),  $\nabla$ <sup>21</sup>,  $\circ$ <sup>23</sup> and  $\triangle$ <sup>24</sup>; e) ChCl:1,3-dimethylurea – ■ (our values), f) ChCl:thiourea – ■ (our values).

The comparison with the literature data (Fig. 1) leads to different conclusions, depending on the type of DES. It should be noted that the slopes of the linear correlations for ChCl:ethylene glycol and ChCl:glycerol, corresponding to the coefficient of volume expansion ( $\beta$ ), are almost the same with those found in the literature.<sup>14,19–22</sup> The density of ChCl:ethylene glycol is slightly lower than the already published ones in the same range of temperature,<sup>14,19–21</sup> while the density

of ChCl:glycerol is slightly higher in the range of 293.15–303.15 K and lower in the range of 313.15–363.15 K than the literature values.<sup>19,20,22</sup> On the other side, the slope of the linear correlation for ChCl:urea differs from the reported one.<sup>21,23,24</sup> The ChCl:urea DES had a moderately lower density in the range of 293.15–343.15 K and a higher density in the range of 353.15–363.15 K than those reported in the literature.<sup>23,24</sup> Also, compared to the values reported by Mjalli and Abdel-Jabbar,<sup>21</sup> the density of ChCl:glycerol and ChCl:urea determined in the present study in the temperature range of 293.15–353.15 K are slightly lower. Since the complete physicochemical and thermodynamic properties of ChCl:propylene glycol, ChCl:1,3-dimethylurea and ChCl:thiourea DESs have not been studied yet, there are no literature data that can be compared with the present ones.

Density is commonly used for the calculation of thermal expansion coefficient,  $\alpha$ , the molecular volume,  $V_m$ , and the lattice energy,  $U_{\text{pot}}$  (see Supplementary material).<sup>27,30</sup> The calculated values of  $V_m$ ,  $U_{\text{pot}}$  and the heat capacity ( $C_p$ ) from equations from the literature<sup>27,30</sup> at 303.15 K are presented in Table S-III of the Supplementary material. The values for lattice energy are similar to those of molten salts; for instance, the fused CsI<sup>31</sup> has the lowest lattice energy among the alkaline halides (613 kJ mol<sup>-1</sup>). This is the primary reason for the liquid state of the studied DESs at the room temperature.

#### *Effect of temperature on dynamic viscosity of the ChCl-based DESs*

Fig. 2 shows the dynamic viscosity ( $\eta$ ) of the prepared ChCl-based DESs as a function of temperature as both the Arrhenius-type and VTF plots along with the literature data for the ChCl:glycerol and ChCl:urea systems (additional considerations are given in Supplementary material). It can be noticed that the DESs have higher viscosity at lower temperatures, which drops rapidly during heating due to the higher mobility of constituents.

At 313.15 K, the viscosity of the tested DESs is in following order: ChCl:1,3-dimethylurea > ChCl:thiourea > ChCl:urea > ChCl:glycerol > ChCl:propylene glycol > ChCl:ethylene glycol. The larger viscosity of the DESs with urea-based compounds indicates the formation of stronger hydrogen bonds in these systems than in the DESs with polyols. Two methyl groups in 1,3-dimethylurea also have the major effect on the viscosity of its DES. The highest viscosity among the polyol-based DESs possesses ChCl:glycerol, as expected, because glycerol has one more –OH group, thus forming stronger H-bonds.  $E_\eta$ -values for the tested DESs are larger than those for the conventional liquids or high temperature molten salts,<sup>32,33</sup> which can be explained by a large ion-to-hole radius ratio in these eutectic mixtures. The differences among the studied DESs in both density and viscosity values can be explained by a better ability of urea to form hydrogen bonds. Ashworth *et al.*<sup>34</sup> indicated that, on average, the individual H-bonds

between urea and choline or even urea with another urea are stronger than those with the chloride. However, urea forms a H-bonded urea[choline]<sup>+</sup> complexed cation that is energetically competitive with [Cl(urea)<sub>2</sub>]<sup>-</sup>.

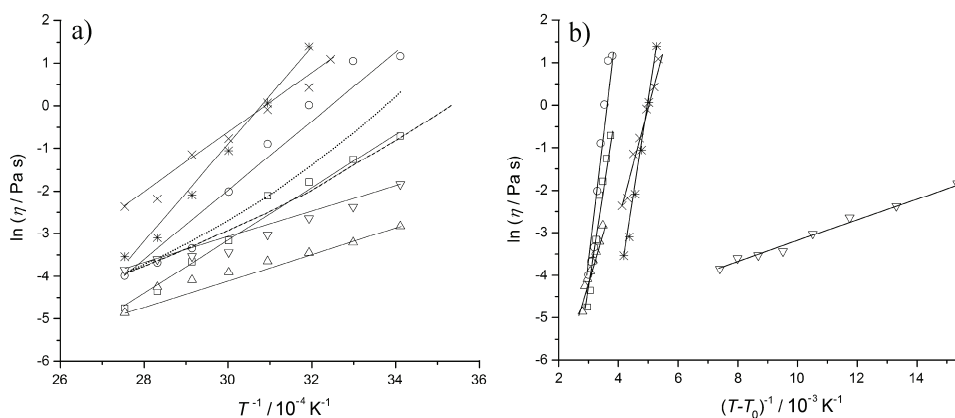


Fig. 2. Temperature dependence of the viscosity ( $\eta$ ) of the studied eutectic mixtures: a) Arrhenius-type plot of viscosity for the DESs; b) VTF plot of viscosity for DESs (ChCl:propylene glycol –  $\nabla$ , ChCl:ethylene glycol –  $\Delta$ , ChCl:glycerol –  $\square$ , ChCl:urea –  $\circ$ , ChCl:1,3-dimethylurea –  $*$  and ChCl:thiourea –  $\times$  (literature data: ChCl:glycerol –  $\cdots$ <sup>22</sup>, ChCl:urea –  $\cdots$ <sup>23</sup>).

It was previously reported<sup>35</sup> that alkyl chain lengthening, or fluorination of organic components causes an increase in van der Waals interactions and hydrogen bonds, which makes ILs more viscous. Since high viscosity at low temperatures can negatively affect any technological process, it is recommended to use the studied DESs at temperatures higher than 313.15 K. The comparison of the calculated  $E_\eta$  values for ChCl:ethylene glycol, ChCl:glycerol and ChCl:urea with the literature shows that they are lower for the first DES<sup>22,23,28,29</sup> but larger for the other two DESs.

For better understanding of the viscous flow, the Eyring's transition state theory is commonly used for calculating the thermodynamic functions of activation from the dynamic viscosity. Usually, the following equation is used to calculate the activation enthalpy change ( $\Delta H^*$ ) and entropy change ( $\Delta S^*$ ) of viscous flow:<sup>27</sup>

$$\ln \frac{\eta V}{h N_A} = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \quad (6)$$

For each DESs system,  $\ln(\eta V/h N_A)$  as a function of  $T^{-1}$  (Eq. (6)) is shown in Fig. 3.

The activation enthalpy ( $\Delta H^*$ ) and entropy changes ( $\Delta S^*$ ) of viscous flow were calculated from the slope and the intercept of the straight lines. The

obtained values of the thermodynamic functions of activation at 313.15 K (since all tested DESs are liquid at this temperature) are listed in Table S-VI of the Supplementary material. The molar enthalpy change of activation for viscous flow is higher than the  $T\Delta S^*$  values. Thus, the energetic contribution which corresponds to the molar enthalpy change of activation for viscous flow is more important than the entropic contribution to the molar Gibbs energy change of activation.

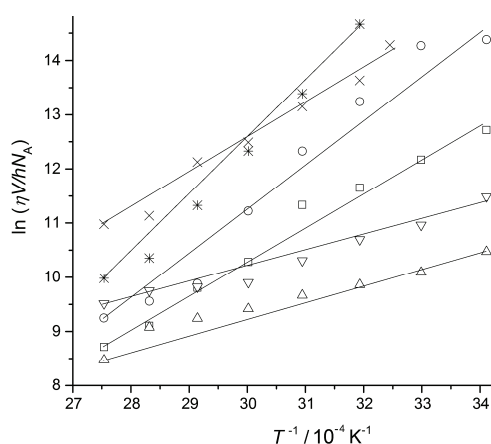


Fig. 3. Plots of  $\ln(\eta V/hN_A)$  against inverse temperature of the studied DESs: ChCl:propylene glycol –  $\nabla$ ; ChCl:ethylene glycol –  $\triangle$ ; ChCl:glycerol –  $\square$ ; ChCl:urea –  $\circ$ , ChCl:1,3-dimethylurea –  $*$  and ChCl:thiourea –  $\times$ .

Based on these results, it can be seen that the ChCl:propylene glycol DES has properties that are similar to those of the ChCl:ethylene glycol and ChCl:glycerol DESs, so it can replace them in the future possible industrial applications or as media for chemical reactions. On the other hand, since the density and viscosity of ChCl:1,3-dimethylurea and ChCl:thiourea DESs are higher than those of the ChCl:urea DES at low temperatures, they can be used in the technological processes at temperatures above 313.15 K.

#### *Effect of temperature on the electrical conductivity of the ChCl-based DESs*

The plots of electrical conductivity as a function of temperature in the temperature range of 303.15–363.15 K for the studied DESs are shown in Fig. 4 (additional considerations are given in Supplementary material).

At 313.15 K, the conductivity of the tested DESs is in following order: ChCl:ethylene glycol > ChCl:propylene glycol > ChCl:glycerol > ChCl:urea > ChCl:thiourea > ChCl:1,3-dimethylurea. The calculated values of both the pre-exponential coefficient ( $A_\kappa$ ) and the activation energy for electrical conductivity ( $E_\kappa$ ) are summarized in Table S-VII of the Supplementary material. Similar values for some ILs were described earlier.<sup>36</sup> The obvious conclusion is that these DESs are conductive, proving the fact that the ionic species are dissociated in the liquid and are able to move independently. However, the temperature dependence



of the measured conductivities of DESs is better correlated with the Vogel–Tamman–Fulcher equation (see Supplementary material).<sup>37</sup>

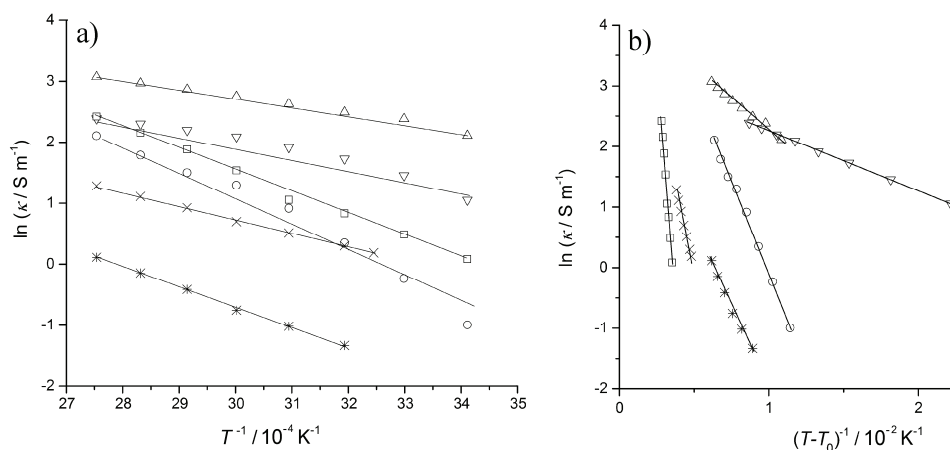


Fig. 4. Temperature dependence of the conductivity ( $\kappa$ ) of the studied eutectic mixtures: a) Arrhenius-type plot of conductivity for the DESs; b) VTF plot of conductivity for DESs (ChCl:propylene glycol ( $\nabla$ ), ChCl:ethylene glycol ( $\Delta$ ), ChCl:glycerol ( $\square$ ), ChCl:urea ( $\circ$ ), ChCl:1,3-dimethylurea – \* and ChCl:thiourea –  $\times$ ).

#### Molar conductivity and viscosity relationship

The  $\log A$ – $\log \eta^{-1}$  relationship is shown in Fig. 5 while the Walden equation coefficients (additional considerations are given in Supplementary material) for the DESs are listed in Table S-X of the Supplementary material.

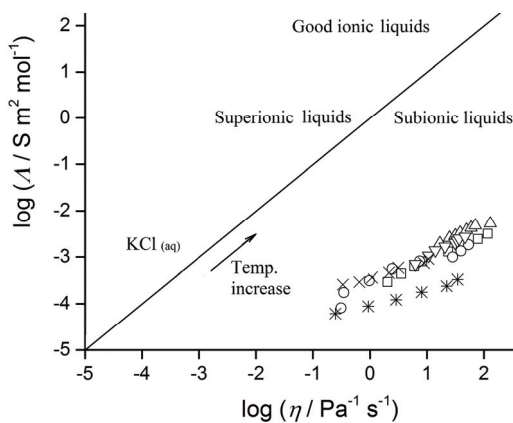


Fig. 5. Application of the fractional Walden rule for the studied DESs (ChCl:propylene glycol –  $\nabla$ ; ChCl:ethylene glycol –  $\Delta$ ; ChCl:glycerol –  $\square$ ; ChCl:urea –  $\circ$ ; ChCl:1,3-dimethylurea – \*; ChCl:thiourea –  $\times$ ).

The  $\alpha'$  values are smaller than 1, as predicted by the ideal Walden rule, implying a progressive raise in the quantity of less conductive ion pairs with heating.<sup>38</sup> When no strong ion-ion interaction is present, the slope is unity. If the

liquid is represented as an ensemble of the independent ions, the Walden plot will be similar to the ideal line.

For the ideal dotted Walden line, the data for the dilute aqueous 0.01 M KCl solution,<sup>39</sup> comprising of equal mobility of fully dissociated ions,<sup>40</sup> were used. Some authors used the  $\Delta W$ -value, the vertical deviation to this ideal line, to characterize DESs.<sup>41</sup> “Good” ILs are fully dissociated and have a  $\Delta W < 1$  while ILs with  $\Delta W = 1$  show 10 % of the ionic conductivity as expected at the ideal (KCl) line. The DESs prepared in the present study have  $\Delta W > 3$ , belonging to the category of “subionic liquids”. From the temperature dependence curves of  $\log A$  vs.  $\log \mu^{-1}$  shown in Fig. 5, it can be seen that the polyol-based DESs are closer to the ideal KCl line than the other DESs. The deviation of the Walden plot from the ideal line for these DESs demonstrates the decreased electrostatic interaction between ChCl and HBD. ChCl:ethylene glycol is the closest to the ideal line, followed by ChCl:glycerol and ChCl:propylene glycol. Among the amide-based DESs, the closest to the ideal line is ChCl:urea, followed by ChCl:thiourea and ChCl:1,3-dimethylurea.

The fractional Walden rule, which states that the activation energy for viscous flow is higher than activation energy for conductivity, finds an interpretation in terms of one of the ionic species being smaller than the other, making them capable of squeezing through smaller gaps in the condensed phase structure. All the studied DESs obey the fractional Walden rule very well and the values of the Walden slope are all smaller than 1 (see Table S-X), indicating the presence of the obvious ion association in the investigated DESs.

From Fig. 5 it is clear that the curves of the studied DESs are below the “ideal” Walden line. The deviation of the Walden plot from the ideal line for these DESs clearly suggests an increased electrostatic interaction between ChCl and the HBD. The second way for calculating the  $\alpha'$  value is the ratio of the temperature-dependent activation energies for viscosity and molar conductivity ( $\alpha' = E_{a,\eta}/E_{a,\sigma} < 1$ ).<sup>38</sup> From these results, it can be concluded that there are not only charge carrying species simply formed by choline and chloride ions in the investigated DESs because all slopes are different. In this case, it is presumed that the conduction involves some degree of cooperation of the ions. Here, it can be seen a resemblance to the process of the viscous flow from molten salts, since in their case the translation of ions of both signs is involved due to the imposed condition of electro-neutrality. In addition, since all the investigated DESs are “subionic”, probably their special accumulation structure also has a role in this phenomenon.

#### *Effect of temperature on the refractive index of the ChCl-based DESs*

For all DESs, the refractive index–temperature relationship is also a linear equation.<sup>19</sup> Refractive index of the tested DESs as a function of temperature is shown in Fig. 6 while the parameters of the linear equations are listed in Table S-XI

of the Supplementary material. For the pure DESs, the refractive index decreases linearly with the increase of temperature, as expected. With the increase of temperature, molecules move more vigorously, so the mixture becomes less dense due to thermal expansion, resulting in the decrease of the refractive index. At 303.15 K, the refractive index of the tested DESs is in following order: ChCl:thiourea > ChCl:urea > ChCl:ethylene glycol > ChCl:glycerol > ChCl:1,3-dimethylurea > ChCl:propylene glycol. For the temperature range of 293.15–363.15 K, the  $n_D$  values for the tested DESs lie within the range of 1.4384–1.5258. By comparing the obtained refractive index data for the ChCl:ethylene glycol and ChCl:glycerol DESs with the literature data, it can be noticed that, at the range of 303.15–333.15 K, higher values were found for the former DES, and slightly lower values for the latter DES.<sup>19</sup> The ranges of the measured refractive index of the prepared DESs are similar to the ranges for the other DESs.<sup>42</sup> At 303.15 K, the phase velocity of the tested DESs is in following order: ChCl:propylene glycol > ChCl:1,3-dimethylurea > ChCl:glycerol > ChCl:ethylene glycol > ChCl:urea > ChCl:thiourea. Ranges for both phase velocity ( $v$ ) and molar refractivity ( $A$ )<sup>43</sup> for the tested DESs are listed in Table S-XII of the Supplementary material.

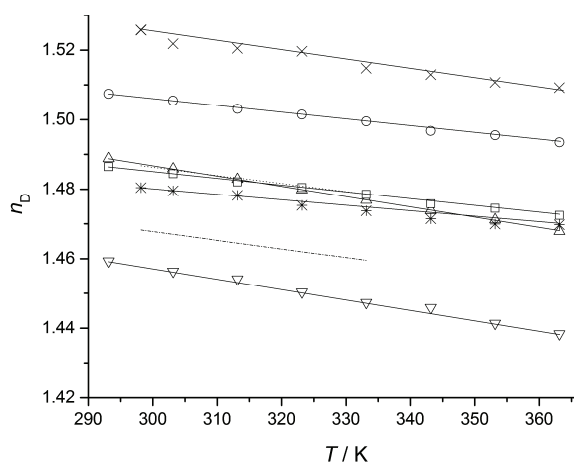


Fig. 6. Temperature dependence of the refractive index of the studied DESs: ChCl:propylene glycol –  $\nabla$  (our values); ChCl:ethylene glycol –  $\triangle$  (our values),  $\cdots$ <sup>19</sup>; ChCl:glycerol –  $\square$  (our values),  $\cdots$ <sup>19</sup>; ChCl:urea –  $\circ$  (our values),  $\cdots$ <sup>19</sup>; ChCl:1,3-dimethylurea –  $*$  (our values) and ChCl:thiourea –  $\times$  (our values).

#### CONCLUSIONS

The ChCl-based DESs with propylene glycol, ethylene glycol, glycerol, urea, 1,3-dimethylurea and thiourea (at 1:2 mole ratios) were prepared. Density, viscosity, electrical conductivity and refractive index of these DESs were measured in the range of 293.15–363.15 K at atmospheric pressure. It was found that density, viscosity and refractive index of the systems decrease with temperature, while electrical conductivity increases. The density and viscosity values were useful in calculating the thermal expansion coefficient, the molecular volume, the lattice energy and the heat capacity of these DESs. After applying the absolute

rate approach of the Eyring theory concerning the viscosity flow, it was noted that the interactional factor was predominant over the structural factor for all the DESs. The viscosity and conductivity values of the tested DESs were fitted by both Arrhenius-type and Vogel–Tamman–Fulcher equation. Also, according to the fractional Walden rule, the density, viscosity and conductivity relationships were set up. The results of this study revealed that the ChCl:propylene glycol DES has the properties similar to the ChCl:ethylene glycol and ChCl:glycerol DESs, thus suggesting them for several possible industrial applications and as media for chemical reactions. However, the properties (density, viscosity and electrical conductivity) of the ChCl:1,3-dimethylurea and ChCl:thiourea DESs are inferior, compared to those of the ChCl:urea DES, but they can be used in processes at temperatures above 313.15 K.

#### SUPPLEMENTARY MATERIAL

Additional data and considerations are available electronically at the pages of the journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

*Acknowledgments.* This paper has been funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project III 45001). The authors would like to thank Dr Jasna Janković from Automotive Fuel Cell Cooperation (Daimler and Ford), National Research Council Canada, and University of British Columbia, Canada. Also, the authors thank Zdravlje Actavis (Leskovac, Serbia) for technical support.

#### ИЗВОД

#### ФИЗИЧКО–ХЕМИЈСКА И ТЕРМОДИНАМИЧКА СВОЈСТВА ЕУТЕКТИЧКИХ РАСТВОРАЧА НА БАЗИ ХОЛИН-ХЛОРИДА

ДРАГАН З. ТРОТЕР<sup>1</sup>, ЗОРАН Б. ТОДОРОВИЋ<sup>1</sup>, ДУШИЦА Р. БОКИЋ-СТОЈАНОВИЋ<sup>2</sup>, БИЉАНА С. ЂОРЂЕВИЋ<sup>1</sup>,  
ВАЊА М. ТОДОРОВИЋ<sup>3</sup>, САНДРА С. КОНСТАНТИНОВИЋ<sup>1</sup> и ВЛАДА Б. ВЕЉКОВИЋ<sup>1</sup>

<sup>1</sup>Технолошки факултет, Универзитет у Нишу, Булевар Ослобођења 124, 16000 Лесковац,

<sup>2</sup>Здравље Активис, Влајкова 199, 16000 Лесковац и <sup>3</sup>Фармацеушки факултет,  
Универзитет у Београду, Војводе Сивце 450, 11221 Београд

У овом раду су описане физичко–хемијска (густина, динамички вискозитет, електрична проводљивост и индекс рефракције) и термодинамичка (коэффициент топлотне експанзије, молекулска запремина, енергија решетке и топлотни капацитет) својства еутектичких растварача холин-хлорид:пропилен гликол, холин-хлорид:1,3-диметилуреа и холин-хлорид:тиоуреа (у молском односу 1:2) на атмосферском притиску у функцији температуре у опсегу 293,15–363,15 К. Ова својства су поређена са својствима неких већ окарактерисаних еутектичких растварача на бази холин-хлорида, и то са холин-хлорид:етилен-гликолом, холин-хлорид:глицеролом и холин-хлорид:уреом (у молском односу 1:2). Густина, вискозитет и индекс рефракције свих еутектичких растварача опадају са порастом температуре, док електрична проводљивост расте. Вискозитет и електрична проводљивост свих припремљених еутектичких растварача су фитоване помоћу једначине Аренијусовог типа и Vogel–Tamman–Fulcher једначине. Промене моларне енталпије, ентропије и Гибсове енергије активације, одређене путем Ејринг теорије, показују да је интеракциони фактор доминантнији у односу на структурни фактор за све еутектичке растварање. Фракционо Walden правило, коришћено је за одређење корелације између моларне проводљивости и вискозитета и резултати показују одличну лине-

арност. Доказано је да еутектички растварач холин-хлорид:пропилен-гликол има својства слична еутектичким растварачима холин-хлорид:етилен гликол и холин-хлорид:глицерол. Међутим, својства еутектичких растварача холин-хлорид:1,3-диметилуреа и холин-хлорид:тиоуреа (густина, динамички вискозитет и електрична проводљивост) су инфериорнија у поређењу са својствима еутектичког растварача холин-хлорид:уреа.

(Примљено 25. фебруара, ревидирано 22. маја, прихваћено 23. маја 2017)

## REFERENCES

1. T. Welton, *Chem. Rev.* **99** (1999) 2071
2. J. F. Brennecke, E. J. Maginn, *AIChE J.* **47** (2001) 2384
3. A. Shariati, K. Gutkowski, C. J. Peters, *AIChE J.* **51** (2005) 1532
4. M. C. Bubalo, S. Vidović, I. Radojčić Redovniković, S. Jokić, *J. Chem. Technol. Biotechnol.* **90** (2015) 1631
5. D. Z. Troter, Z. B. Todorović, D. R. Đokić-Stojanović, O. S. Stamenković, V. B. Veljković, *Renew. Sustain. Energy Rev.* **61** (2016) 473
6. K. M. Docherty, C. F. Kulpa, *Green Chem.* **7** (2005) 185-189.
7. D. Zhao, Y. Liao, Z. Zhang, *Clean-Soil Air Water* **35** (2007) 42
8. A. P. Abbott, D. Boothby, G. Capper, D. L. Davies, R. K. Rasheed, *J. Am. Chem. Soc.* **126** (2004) 9142
9. M. Avalos, R. Babiano, P. Cintas, J. L. Jimenez, J. C. Palacios, *Angew. Chem. Int. Ed.* **45** (2006) 3904
10. H. G. Morrison, C. C. Sun, S. Neervannan, *Int. J. Pharm.* **378** (2009) 136
11. A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, V. Tambyrajah, *Chem. Commun.* **1** (2003) 70
12. J. K. Blusztajn, *Science* **281** (1998) 794.
13. S. S. Konstantinović, B. R. Danilović, J. T. Ćirić, S. B. Ilić, D. S. Savić, V. B. Veljković, *Chem. Ind. Chem. Eng. Q.* **22** (2016) 461
14. K. Shahbaz, F. S. Mjalli, M. A. Hashim, I. M. AlNashef, *Thermochim. Acta* **515** (2011) 67
15. K. Shahbaz, F. S. Mjalli, M. A. Hashim, I. M. AlNashef, *Fluid Phase Equilib.* **319** (2012) 48
16. K. Shahbaz, F. S. Mjalli, M. A. Hashim, I. M. Al-Nashef, *Fluid Phase Equilib.* **354** (2013) 304
17. F. S. Mjalli, K. Shahbaz, I. M. AlNashef, *Thermochim. Acta* **614** (2015) 185
18. S. Mjalli, *Fluid Phase Equilib.* **409** (2016) 312
19. R. B. Leron, A. N. Soriano, M. H. Li, *J. Taiwan Inst. Chem. Eng.* **43** (2012) 551
20. K. Shahbaz, S. Baroutian, F. S. Mjalli, M. A. Hashim, I. M. Al-Nashef, *Thermochim. Acta* **527** (2012) 59
21. F. Mjalli, N. M. Abdel-Jabbar, *Fluid Phase Equilib.* **381** (2014) 71
22. A. Yadav, S. Trivedi, R. Rai, S. Pandey, *Fluid Phase Equilib.* **367** (2014) 135
23. A. Yadav, S. Pandey, *J. Chem. Eng. Data* **59** (2014) 2221
24. R. B. Leron, M. H. Li, *J. Chem. Thermodyn.* **54** (2012) 293
25. J. Jacquemin, P. Husson, A. A. H. Padua, V. Majer, *Green Chem.* **8** (2006) 172
26. H. Rodriguez, J. F. Brennecke, *J. Chem. Eng. Data* **51** (2006) 2145
27. V. Constantin, A. K. Adya, A.-M. Popescu, *Fluid Phase Equilib.* **395** (2015) 58
28. A. M. Popescu, V. Constantin, A. Florea, A. Baran, *Rev. Chim.* **62** (2011) 531
29. O. Ciocirlan, O. Iulian, O. Croitoru, *Rev. Chim.* **61** (2010) 721
30. L. Glasser, *J. Solid State Chem.* **206** (2013) 139

31. W. M. Haynes, *CRC Handbook of chemistry and physics, A ready reference book of chemical and physical data*, 94<sup>th</sup> ed., CRC Press, Taylor & Francis Group, Boca Raton, FL, 2013, pp. 12–21
32. A. M. Popescu, *Rev. Chim.* **44** (1999) 765
33. G. J. Janz, R. P. T. Tomkins, C. B. Allen, J. R. Downey, G. L. Gardner, U. Krebs, S.K. Singer, *J. Phys. Chem. Ref. Data* **4** (1975) 871
34. C. R. Ashworth, R. P. Matthews, T. Welton, P. A. Hunt, *Phys. Chem. Chem. Phys.* **18** (2016) 18145
35. P. Bonhöte, A. P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* **35** (1996) 1168
36. S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, *J. Phys. Chem. Ref. Data* **35** (2006) 1475
37. I-W. Sun, Y.-C. Lin, B.-K. Chen, C.-W. Kuo, C.-C. Chen, S.-G. Su, P.-R. Chen, T.-Y. Wu, *Int. J. Electrochem. Sci.* **7** (2012) 7206
38. C. A. Angell, W. Xu, M. Yoshizawa-Fujita, A. Hayashi, J.-P. Belieres, P. Lucas, M. Videa, Z.-F. Zhao, K. Ueno, Y. Ansari, J. Thomson, D. Gervasio, in: *Electrochemical aspects of ionic liquids*, H. Ohno (Ed.), John Wiley & Sons, Inc., Hoboken, NJ, 2011, pp. 5–33
39. M. Yoshizawa, W. Xu, C. A. Angell, *J. Am. Chem. Soc.* **125** (2003) 15411
40. T. Y. Wu, S.-G. Su, Y. C. Lin, H. P. Wang, M. W. Lin, S. T. Gung, I. W. Sun, *Electrochim. Acta* **56** (2010) 853
41. D. Rengstl, V. Fischer, W. Kunz, *Phys. Chem. Chem. Phys.* **16** (2014) 22815
42. F. Chemat, H. Anjum, A. M. Shariff, P. Kumar, T. Murugesan, *J. Mol. Liq.* **218** (2016) 301
43. M. Born, E. Wolf, *Principles of Optics: Electromagnetic theory of propagation, interference and diffraction of light*, 7th ed., Cambridge University Press, Cambridge, 1999, pp. 11–14.