



SUPPLEMENTARY MATERIAL TO

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

DRAGAN Z. TROTTER<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

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

EFFECT OF TEMPERATURE ON DENSITY OF THE ChCl-BASED DESs

A very good linear correlation between density and temperature was observed for all DESs systems studied, *i.e.*:

$$\rho = a + bT \quad (1)$$

where  $\rho$  is the density ( $\text{kg m}^{-3}$ ),  $T$  is the absolute temperature (K),  $a$  is the density at 0 K ( $\text{kg m}^{-3}$ ) and  $b$  is the coefficient of volume expansion (in  $\text{g m}^{-3} \text{K}^{-1}$ ). The parameters of Eq. (1) for the studied DESs, along with density ranges, mean relative percent deviation (*MRPD*) and the coefficients of determination ( $R^2$ ) are presented in Table S-I. Very low *MRPD*-values and  $R^2$ -values close to unity confirm the good linear dependence of density on temperature.

The thermal expansion coefficient was calculated from the linear  $\ln \rho - T$  plot:<sup>1</sup>

$$\ln \rho = c - aT \quad (2)$$

where  $c$  represents an empirical constant. The thermal expansion coefficient describes a tendency of a fluid to expand with an increase in temperature and to contract when cooled. Higher thermal expansion coefficient values correlate with the larger free volumes, which create additional space between the unbound molecules, thus decreasing density. When heated, the kinetic energy of the molecules increases, the molecules spread further, causing undesirable expansions.<sup>2</sup> Higher content of HBD in DES increases the hydrogen bond interactions between the molecules, also increases the density and reduces the free volume, resulting in lowering the thermal expansion coefficient.<sup>3</sup>

\* Corresponding author. E-mail: veljkovicvb@yahoo.com

TABLE S-I. Parameters of Eq. (1) in the temperature range of 293.15–363.15 K

DES	Density range, kg m <sup>-3</sup>	<i>a</i> / kg m <sup>-3</sup>	<i>b</i> / kg m <sup>-3</sup> K <sup>-1</sup>	<i>MRPD</i> / %	<i>R</i> <sup>2</sup>
ChCl:propylene glycol	1156.0–1191.0	1331.3	−0.482	±0.05	0.993
ChCl:ethylene glycol	1064.0–1109.0	1293.3	−0.629	±0.05	0.997
ChCl:glycerol	1147.4–1195.1	1402.2	−0.707	±0.13	0.989
ChCl:urea	1161.1–1182.9	1269.0	−0.298	±0.07	0.985
ChCl:1,3-dimethylurea <sup>a</sup>	1061.2–1362.6	3168.0	−5.7929	±0.60	0.990
ChCl:thiourea <sup>b</sup>	1170.9–1361.3	2409.4	−3.4017	±0.29	0.993

<sup>a</sup>313.15–363.15 K; <sup>b</sup>308.15–363.15 K

As shown in Table S-II, the values of the thermal expansion coefficients are in the range of  $3 \times 10^{-4}$ – $48 \times 10^{-4}$  K<sup>-1</sup>, which is similar to the range for other DESs.<sup>1,2,4,5</sup> The studied DESs do not expand appreciably in the investigated temperature range.

TABLE S-II. Parameters of Eq. (2) in the temperature range of 293.15–363.15 K

DES	<i>c</i> / kg m <sup>-3</sup> K <sup>-1</sup>	<i>α</i> × 10 <sup>4</sup> / K <sup>-1</sup>	<i>MRPD</i> / %	<i>R</i> <sup>2</sup>
ChCl:propylene glycol	7.2023	4	±0.05	0.993
ChCl:ethylene glycol	7.1810	6	±0.09	0.997
ChCl:glycerol	7.2629	6	±0.02	0.990
ChCl:urea	7.1493	3	±0.21	0.985
ChCl:1,3-dimethylurea <sup>a</sup>	8.7166	48	±0.09	0.991
ChCl:thiourea <sup>b</sup>	8.0453	27	±0.06	0.991

<sup>a</sup>313.15–363.15 K; <sup>b</sup>308.15–363.15 KTABLE S-III. The calculated values of *V*<sub>m</sub>, *U*<sub>pot</sub> and *C*<sub>p</sub> for the prepared DESs at 303.15 K

DES	<i>V</i> <sub>m</sub> / nm <sup>3</sup>	<i>U</i> <sub>pot</sub> / kJ mol <sup>-1</sup>	<i>C</i> <sub>p</sub> / J mol <sup>-1</sup>
ChCl:propylene glycol	0.409	1156.7	469.8
ChCl:ethylene glycol	0.397	1169.8	457.5
ChCl:glycerol	0.451	1113.8	513.5
ChCl:urea	0.365	1208.0	424.4
ChCl:1,3-dimethylurea <sup>a</sup>	0.385	1184.7	444.1
ChCl:thiourea <sup>b</sup>	0.356	1220.6	414.2

<sup>a</sup>313.15 K; <sup>b</sup>308.15 K

In general, the viscosity of the binary DESs is affected by the strength of the salt–HBD interactions, namely van der Waals interactions, electrostatic interactions and hydrogen bonds present in the molecular structure. The temperature variation of the viscosity of ILs follows the Arrhenius-type equation<sup>6</sup> or Vogel–Tamman–Fulcher (VTF) equation<sup>6</sup> and the same can be applied for DESs. As stated elsewhere,<sup>7</sup> the viscosity–temperature relationship can be fitted by the Arrhenius-type equation, which is a simplified version of Eyring’s absolute rate theory:<sup>8</sup>

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right) \text{ or } \ln \eta = \ln \eta_0 + \frac{E_\eta}{RT} \quad (3)$$

where  $\eta$  is the viscosity,  $T$  is the absolute temperature,  $E_\eta$  is the activation energy,  $\eta_0$  is a constant and  $R$  is the universal gas constant. The viscosity–temperature dependence was fitted by the Arrhenius-type equation<sup>8–10</sup> for the studied DESs, as shown in Table S-IV.

TABLE S-IV. Arrhenius-type equations for viscosity data of the DESs studied over the temperature range 293.15–363.15 K

DES	Viscosity range Pa s	Viscosity Arrhenius equation ( $\eta$ / Pa s)	$A_\eta \times 10^6$ Pa s	$E_\eta$ J mol <sup>-1</sup>	MRPD %	$R^2$
ChCl:propylene glycol	0.021–0.159	$\ln \eta = 2984.7T^{-1} - 12.2$	5.14	24815	±3.45	0.966
ChCl:ethylene glycol	0.007–0.059	$\ln \eta = 2736.8T^{-1} - 12.2$	5.23	22754	±2.10	0.963
ChCl:glycerol	0.008–0.490	$\ln \eta = 6376.3T^{-1} - 22.3$	2.16	53013	±8.13	0.983
ChCl:urea	0.018–3.195	$\ln \eta = 8987.6T^{-1} - 29.0$	2.58	74723	±19.72	0.968
ChCl:1,3-dimethylurea <sup>a</sup>	0.029–4.029	$\ln \eta = 11489T^{-1} - 35.5$	4.01	95520	±15.82	0.991
ChCl:thiourea <sup>b</sup>	0.094–2.972	$\ln \eta = 6971.9T^{-1} - 21.7$	3.88	57964	±14.44	0.984

<sup>a</sup>313.15–363.15 K; <sup>b</sup>308.15–363.15 K

Because of the deviation from the Arrhenius-type equation, Vogel–Tammann–Fulcher (VTF) equation should be more appropriate:<sup>7</sup>

$$\eta = \eta_0 \exp\left(\frac{B_\eta}{T - T_0}\right) \quad (5)$$

where  $\eta_0$ ,  $B_\eta$ , and  $T_0$  represent the adjustable parameter, the factor related to the activation energy, and the so-called ideal glass-transition temperature, respectively;<sup>11</sup> their values are shown in Table S-V.

TABLE S-V. The adjustable parameters of VTF equation parameters of viscosity over the temperature range 293.15–363.15 K

DES	VTF equation	$\eta_0$ Pa s	$B_\eta$ K	$T_0$ K	MRPD %	$R^2$
ChCl:propylene glycol	$\ln \eta = 252.0(T - T_0)^{-1} - 5.7$	$3.348 \times 10^{-3}$	252.0	228	±1.61	0.990
ChCl:ethylene glycol	$\ln \eta = 2636.3(T - T_0)^{-1} - 12.01$	$6.107 \times 10^{-6}$	2636	6	±2.10	0.964
ChCl:glycerol	$\ln \eta = 5393(T - T_0)^{-1} - 20.68$	$1.044 \times 10^{-9}$	5393	26	±8.42	0.983
ChCl:urea	$\ln \eta = 7400(T - T_0)^{-1} - 26.43$	$3.32 \times 10^{-12}$	7400	30	±20.16	0.968
ChCl:1,3-dimethylurea <sup>a</sup>	$\ln \eta = 4579(T - T_0)^{-1} - 22.91$	$1.127 \times 10^{-10}$	4579	124	±9.57	0.995
ChCl:thiourea <sup>b</sup>	$\ln \eta = 2819(T - T_0)^{-1} - 14.07$	$7.753 \times 10^{-7}$	2819	121	±18.73	0.984

<sup>a</sup>313.15–363.15 K; <sup>b</sup>308.15–363.15 K

TABLE S-VI. The thermodynamic functions of activation of viscous flow, as well as the values of  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  at 313.15 K, for the tested DESs

DES	Eyring's Equation	$R^2$	$\Delta H^*$ J mol <sup>-1</sup>	$T\Delta S^*$ kJ mol <sup>-1</sup>	$\Delta G^*$ kJ mol <sup>-1</sup>
ChCl:propylene glycol	$\ln(\eta V/hN_A) = 2941.0T^{-1} + 1.3$	0.965	24.5	-3.4	27.9
ChCl:ethylene glycol	$\ln(\eta V/hN_A) = 2675.2T^{-1} + 1.3$	0.962	22.2	-3.5	25.7
ChCl:glycerol	$\ln(\eta V/hN_A) = 6311.7T^{-1} - 8.6$	0.983	52.5	22.4	30.1
ChCl:urea	$\ln(\eta V/hN_A) = 8960.4T^{-1} - 15.7$	0.968	74.5	40.8	33.7
ChCl:1,3-dimethylurea	$\ln(\eta V/hN_A) = 10944T^{-1} - 20.4$	0.989	91.0	53.2	37.8
ChCl:thiourea	$\ln(\eta V/hN_A) = 6673.2T^{-1} - 7.5$	0.983	55.5	19.5	36.0

TABLE S-VII. Arrhenius-type equations for conductivity data with calculated pre-exponential factors and activation energies for DESs over the temperature range 293.15–363.15 K

DES	Conductivity range, S m <sup>-1</sup>	Conductivity, Arrhenius-type equation ( $\kappa$ /S m <sup>-1</sup> )	$A_\kappa$ S m <sup>-1</sup>	$E_\kappa$ J mol <sup>-1</sup>	MRPD %	$R^2$
ChCl:propylene glycol	2.860–10.870	$\ln \kappa = -1948.6T^{-1} + 7.8$	2584	16200	±4.72	0.957
ChCl:ethylene glycol	8.260–21.550	$\ln \kappa = -1391.4T^{-1} + 6.9$	1012	11568	±0.95	0.989
ChCl:glycerol	1.088–11.227	$\ln \kappa = -3590.8T^{-1} + 12.3$	220356	29853	±7.50	0.995
ChCl:urea	0.369–8.220	$\ln \kappa = -4574.1T^{-1} + 14.8$	2808047	38029	±13.68	0.976
ChCl:1,3-dimethylurea <sup>a</sup>	0.264–1.119	$\ln \kappa = -3307.8T^{-1} + 9.2$	10055.7	27501	±3.13	0.998
ChCl:thiourea <sup>b</sup>	1.204–3.612	$\ln \kappa = -2240.5T^{-1} + 7.4$	1718.1	18627.5	±1.83	0.999

<sup>a</sup>313.15–363.15 K; <sup>b</sup>308.15–363.15 K

The relationship between viscosity and conductivity is well-known:<sup>12</sup> the larger the viscosity, the lower the conductivity. Thus, the electrical conductivity increases with increasing the temperature.

The electrical conductivity of the tested DESs is fitted by the Arrhenius-type equation:<sup>1,13</sup>

$$\ln \kappa = \ln \kappa_0 - \frac{E_\kappa}{RT} \quad (7)$$

where  $T$  is the absolute temperature,  $\kappa_0$  is a constant and  $E_\kappa$  is the activation energy for conduction.

The temperature dependence of the measured conductivities of DESs is better correlated with the Vogel–Tamman–Fulcher equation:<sup>7</sup>

$$\kappa = \kappa_0 \exp\left(\frac{-B_\kappa}{T - T_0}\right) \quad (8)$$

where  $\kappa_0$  is the fitting parameter,  $B_\kappa$  is a factor associated with the activation energy<sup>11</sup> and  $T_0$  is related to the ideal glass-transition temperature.<sup>11,14</sup> The best fit values for the VTF fitting parameters are summarized in Table S-VIII. The pre-exponential factor  $\kappa_0$  relates to the number of mobile charge carriers in the DESs. The ChCl:glycerol DES has the highest  $\kappa_0$  value of  $1.576 \times 10^5 \text{ S m}^{-1}$  due to its enhanced ion dissociation by the polar glycerol, while ChCl:propylene glycol DES has the lowest  $\kappa_0$  value of  $25.5 \text{ S m}^{-1}$  due to the formation the polypropylene glycols, so the ion mobility is reduced.

TABLE S-VIII. VTF equation parameters of conductivity

DES	VTF equation	$\kappa_0$ S m <sup>-1</sup>	$B_\kappa$ K	$T_0$ K	MRPD %	$R^2$
ChCl:propylene glycol	$\ln \kappa = -98.52(T-T_0)^{-1} + 3.2381$	25.5	98.52	248.1	±0.34	0.999
ChCl:ethylene glycol	$\ln \kappa = -196.76(T-T_0)^{-1} + 4.2603$	70.83	196.76	201.0	±0.75	0.994
ChCl:glycerol	$\ln \kappa = -3375.5(T-T_0)^{-1} + 11.968$	157629.1	3375.5	9.9	±7.81	0.995
ChCl:urea	$\ln \kappa = -601.12(T-T_0)^{-1} + 5.9321$	376.9	601.12	205.7	±4.27	0.996
ChCl:1,3-dimethylurea <sup>a</sup>	$\ln \kappa = -527.38(T-T_0)^{-1} + 3.3153$	27.5	527.38	201.0	±11.63	0.992
ChCl:thiourea <sup>b</sup>	$\ln \kappa = -1086.9(T-T_0)^{-1} + 5.4118$	224.03	1086.9	100.8	±3.07	0.998

<sup>a</sup>313.15–363.15 K; <sup>b</sup>308.15–363.15 K

Molar conductivity of the DESs ( $A$ ) was calculated by using the equation:

$$A = \frac{\kappa M}{\rho} \quad (9)$$

where  $M$ ,  $\kappa$  and  $\rho$  are the molar mass, conductivity and density of the DESs, respectively. The observed temperature dependences of molar conductivity are fitted by the empirical VTF equation:

$$A = A_0 \exp\left(\frac{-B_A}{T - T_0}\right) \quad (10)$$

where  $A_0$ ,  $B_A$  and  $T_0$  are the fitting parameters. Their values are tabulated in Table S-IX while the VTF plot of molar conductivity for DESs is represented in Fig. S-1.

TABLE S-IX. VTF equation parameters of molar conductivity

DES	VTF equation	$A_0$ S m <sup>2</sup> mol <sup>-1</sup>	$B_A$ K	$T_0$ K	MRPD %	$R^2$
ChCl:propylene glycol	$\ln A = -94.693 \cdot (T-T_0)^{-1} - 5.074$	0.0063	94.693	250	±0.13	0.999
ChCl:ethylene glycol	$\ln A = -280.42 \cdot (T-T_0)^{-1} - 3.710$	0.0245	280.42	181	±0.31	0.995
ChCl:glycerol	$\ln A = -3218.4(T-T_0)^{-1} + 3.617$	37.237	3218.4	20	±0.52	0.995
ChCl:urea	$\ln A = -370.84(T-T_0)^{-1} - 3.567$	0.0282	370.84	230	±0.59	0.998

TABLE S-IX. Continued

DES	VTF equation	$A_0$ S m <sup>2</sup> mol <sup>-1</sup>	$B_A$ K	$T_0$ K	MRPD %	$R^2$
ChCl:1,3-dimethylurea <sup>a</sup>	$\ln A = -3408.2(T-T_0)^{-1} + 1.905$	6.7212	3408.2	20	±0.16	0.999
ChCl:thiourea <sup>b</sup>	$\ln A = -2243.1(T-T_0)^{-1} - 0.491$	0.6122	2243.1	20	±0.17	0.999

<sup>a</sup>313.15–363.15 K; <sup>b</sup>308.15–363.15 K

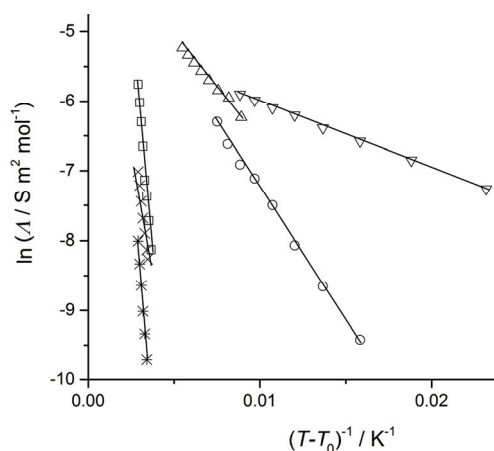


Fig. S-1. VTF plot of molar conductivity for DESs (ChCl:propylene glycol –  $\nabla$ , ChCl:ethylene glycol –  $\Delta$ , ChCl:glycerol –  $\square$ , ChCl:urea –  $\circ$ , ChCl:1,3-dimethylurea –  $*$  and ChCl:thiourea –  $\times$ ).

The relation between the mobility of ions and viscosity is given by the Walden rule:

$$\lambda\eta = \text{const.} \quad (11)$$

where  $\lambda$  is the equivalent conductivity. If the dissociation of a solute in an electrolytic solution is not known, the molar conductivity is used instead of the equivalent conductivity. The Walden rule is helpful in organizing and classifying the ILs.<sup>15</sup> The Walden plot that correlates the molar conductivity with the temperature-dependent fluidity (in its  $\log A - \log \eta^{-1}$  form) is used as a classification diagram in order to distinguish the “good” ILs, “poor” ILs, “superionic” liquids *etc.*<sup>1,15,16</sup> The “fractional” Walden rule is more appropriate to be used for molten salts and ILs, written as:

$$A\eta^{\alpha'} = C \text{ or } \log A = \log C + \alpha' \log \eta^{-1} \quad (12)$$

where  $C$  is the Walden product (temperature-dependent constant),  $\eta^{-1}$  is the fluidity and  $\alpha'$  is a positive constant that represents the slope of the line in the Walden plot, and reflects on the decoupling of the ions.<sup>11</sup> The parameter  $\alpha'$  shows the difference of the activation energies of the ionic conductivity and viscosity.<sup>16–18</sup> For the glass forming molten zinc chloride, Eq. (13) was found to

be valid within a broad range (four orders of magnitude) of conductivities and viscosities, with the constant  $\alpha'$  of roughly 0.8.<sup>19</sup>

TABLE S-X. Walden equation coefficients with MRPD and  $R^2$  for the DESs over the temperature range 293.15–363.15 K

DES	$\alpha' \times 10^2$	$C \times 10^4$	MRPD / %	$R^2$
ChCl:propylene glycol <sup>a</sup>	66.54	2.18	±0.64	0.987
ChCl:ethylene glycol <sup>b</sup>	51.21	5.00	±0.96	0.956
ChCl:glycerol <sup>c</sup>	56.81	2.17	±0.73	0.994
ChCl:urea <sup>d</sup>	48.91	2.51	±3.02	0.920
ChCl:1,3-dimethylurea <sup>e</sup>	33.18	0.92	±0.68	0.987
ChCl:thiourea <sup>f</sup>	35.84	3.63	±0.68	0.983

<sup>a</sup> $\log A = 0.6654 \log \eta^{-1} - 3.6612$ ; <sup>b</sup> $\log A = 0.5121 \log \eta^{-1} - 3.3006$ ; <sup>c</sup> $\log A = 0.5681 \log \eta^{-1} - 3.6631$ ; <sup>d</sup> $\log A = 0.4891 \log \eta^{-1} - 3.5997$ ; <sup>e</sup> $\log A = 0.3318 \log \eta^{-1} - 4.0384$ ; <sup>f</sup> $\log A = 0.3584 \log \eta^{-1} - 3.4401$

TABLE S-XI. Parameters of the  $n_D$  equation for the tested DESs in the range 293.15–363.15 K

DES	$n_D$ range	Intercept	Slope	MRPD / %	$R^2$
ChCl:propylene glycol	1.438–1.459	1.547	–0.0003	±4.10	0.994
ChCl:ethylene glycol	1.467–1.488	1.576	–0.0003	±3.99	0.999
ChCl:glycerol	1.472–1.486	1.545	–0.0002	±2.71	0.997
ChCl:urea <sup>a</sup>	1.493–1.507	1.566	–0.0002	±2.67	0.997
ChCl:1,3-dimethylurea <sup>a</sup>	1.469–1.480	1.5338	–0.0002	±0.46	0.977
ChCl:thiourea <sup>b</sup>	1.509–1.525	1.6019	–0.0003	±0.89	0.974

<sup>a</sup>Temperature range: 303.15–363.15 K, 298.15–363.15 K

TABLE S-XII. The phase velocity ( $v$ ) and the molar refractivity ( $A$ ) for the prepared DESs in the temperature range of 293.15–363.15 K

DES	$v / 10^7 \text{ m s}^{-1}$	$A / 10^{-6} \text{ m}^3 \text{ mol}^{-1}$
ChCl:propylene glycol	20.56–20.86	66.30–67.02
ChCl:ethylene glycol	20.15–20.44	68.62–68.89
ChCl:glycerol	20.18–20.37	77.85–79.09
ChCl:urea	19.90–20.09	65.06–65.39
ChCl:1,3-dimethylurea <sup>a</sup>	20.26–20.41 <sup>a</sup>	65.64–83.00 <sup>b</sup>
ChCl:thiourea <sup>b</sup>	19.66–19.87 <sup>a</sup>	66.11–74.45 <sup>b</sup>

<sup>a</sup>298.15–363.15 K, <sup>b</sup>313.15–363.15 K

## ADDITIONAL INFORMATION ON ChCl-BASED DESs

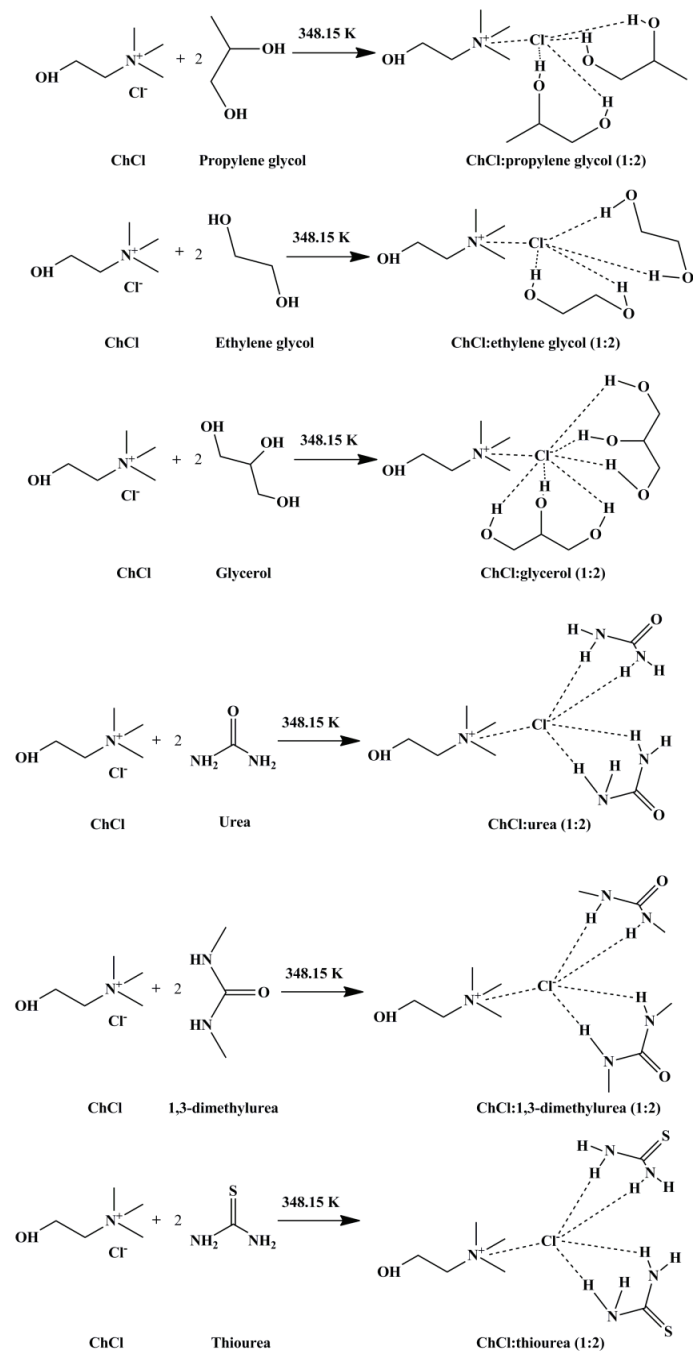


Fig. S-2. Schematic presentation of the ChCl-based DESs preparation.



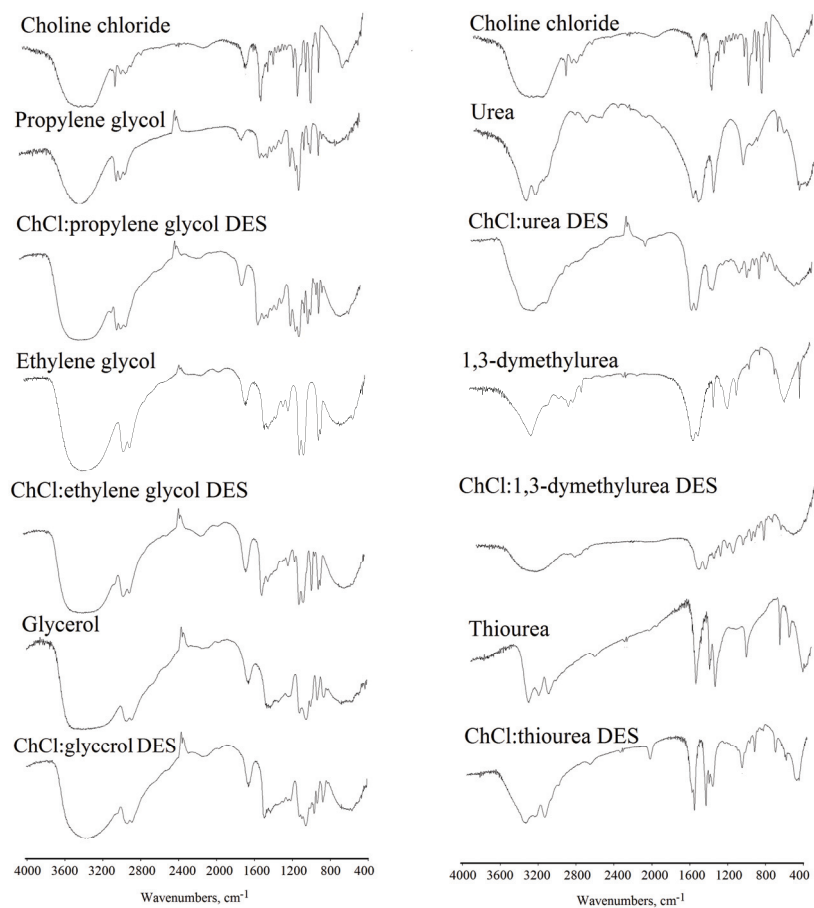


Fig. S-3. FTIR spectra of ChCl, propylene glycol, ChCl:propylene glycol DES, ethylene glycol, ChCl:ethylene glycol DES, glycerol, ChCl:glycerol DES, urea, ChCl:urea DES, 1,3-dimethylurea, ChCl:1,3-dimethylurea DES, thiourea and ChCl:thiourea DES.

*FTIR spectra discussion.* The spectra of ChCl shows very strong and broad band at  $3406\text{ cm}^{-1}$ , which belongs to  $\nu(\text{OH})$  stretching vibration. The shape of the band indicates the presence of hydrogen bond, probably intramolecular, since ChCl molecule possesses both hydrogen bonding donors and acceptors. Also, the weak peak at  $2846\text{ cm}^{-1}$  confirms existence of hydrogen bonds.<sup>20</sup> The band at  $3247\text{ cm}^{-1}$  belongs to  $\nu(\text{NH}_3^+)$  vibrations, typical for charged amine derivatives, while the appropriate deformation vibration  $\delta(\text{NH}_3^+)$  appears at  $1660\text{ cm}^{-1}$ .<sup>21</sup> The FTIR spectra of ChCl-based DESs with propylene glycol, ethylene glycol and glycerol show a strong and broad band at  $\sim 3400\text{ cm}^{-1}$  which is understandable,

considering the presence of hydroxyl groups in all compounds. The shape of band suggests hydrogen bonded hydroxyl functional group, which covers all bands belonging to amine vibrations form ChCl. These spectra are very difficult to discuss, considering the overlapping of amine and hydroxyl bands, but spectra of all DESs possess all bands typical for ChCl and used alcohols.

FTIR spectra of the DES of ChCl with urea show a strong and broad band at  $\sim 3400\text{ cm}^{-1}$  which, as in ChCl spectra, belongs to hydrogen bonded hydroxyl functional group. The DES of ChCl and urea possesses a band of charged amine derivatives slightly moved at  $3334$  and  $3205\text{ cm}^{-1}$ , which is expected, considering its suggested structure. On the other hand, the spectrum of DES does not have a vibration at  $1684\text{ cm}^{-1}$ , which can be found in the spectra of urea. This position is characteristic for carbonyl  $\nu(\text{C}=\text{O})$  vibration, suggesting the enol tautomeric form of urea in this DES. As reported elsewhere<sup>22</sup> the spectra of ChCl DESs with thiourea and 1,3-dimethylurea also has a strong and broad band at  $\sim 3400\text{ cm}^{-1}$  which, as in ChCl spectra, belongs to the hydrogen bonded hydroxyl functional group. FTIR spectrum of 1,3-dimethylurea has a stretching vibration at  $3345\text{ cm}^{-1}$ , which corresponds to secondary  $\nu(\text{NH})$  group. Bands at  $2344$  and  $1837\text{ cm}^{-1}$  come from stretching  $\nu(\text{C}=\text{NH}^+)$  and deformation  $\delta(\text{C}=\text{NH}^+)$  vibrations, which confirms that the 1,3-dimethylurea is in its imidic acid form ((*Z*)-*N,N'*-dimethyl-carbamimidic acid). The band belonging to stretching  $\nu(\text{OH})$  vibration is widely broad at  $3378\text{ cm}^{-1}$  and covers all the amine vibrations' belonging bands.  $\nu(\text{C}-\text{O})$  vibration in DES is slightly moved for  $\Delta\nu = 11\text{ cm}^{-1}$  in DES's spectrum, mostly because of choline-1,3-dimethylurea interaction. The FTIR spectrum of thiourea possesses asymmetrical and symmetrical stretching vibrations  $\nu_{\text{as}}(\text{NH}_2) + \nu_{\text{s}}(\text{NH}_2)$  at  $3380$  and  $3273\text{ cm}^{-1}$ , as well as  $\text{N}-\text{C}=\text{S}$  I,  $\text{N}-\text{C}=\text{S}$  II and  $\text{N}-\text{C}=\text{S}$  III bands at  $1436$ ,  $1399$  and  $1084\text{ cm}^{-1}$ , proving that thiourea is in its thiol form (carbamimid-othioic acid).<sup>23</sup> The slight shift of amine deformational vibrations ( $\Delta\nu = 11\text{ cm}^{-1}$ ) is also explained by choline–thiourea interaction).

#### REFERENCES

1. V. Constantin, A. K. Adya, A.-M. Popescu, *Fluid Phase Equilib.* **395** (2015) 58
2. F. Chemat, H. Anjum, A. M. Shariff, P. Kumar, T. Murugesan, *J. Mol. Liq.* **218** (2016) 301
3. C. Florindo, F. S. Oliveira, L. P. N. Rebelo, A. M. Fernandes, I. M. Marrucho, *ACS Sustainable Chem. Eng.* **2** (2014) 2416
4. O. Ciocirlan, O. Iulian, O. Croitoru, *Rev. Chim.* **61** (2010) 721
5. F. Chemat, H. J. You, K. Muthukumar, T. Murugesan, *J. Mol. Liq.* **212** (2015) 605
6. O. O. Okoturo, T. J. Van der Noot, *J. Electroanal. Chem.* **568** (2004) 167
7. 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
8. J. Jacquemin, P. Husson, A. A. H. Padua, V. Majer, *Green Chem.* **8** (2006) 172
9. A. M. Popescu, *Rev. Chim.* **44** (1999) 765
10. G. J. Janz, R. P. T. Tomkins, C. B. 654 Allen, J. R. Downey, G. L. Gardner, U. Krebs, S.K. Singer, *J. Phys. Chem. Ref. Data* **4** (1975) 871

11. 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
12. A. García, S. Aparicio, R. Ullah, M. Atilhan, *Energy fuels* **29** (2015) 2616
13. A. M. Popescu, V. Constantin, A. Florea, A. Baran, *Rev. Chim.* **62** (2011) 531
14. M. Aniya, M. Ikeda, *Materials* **3** (2010) 5246
15. W. Xu, E. I. Cooper, C. A. Angell, *J. Phys. Chem. B* **107** (2003) 6170
16. C. A. Angell, in: M. Gaune-Escard, K.R. Seddon (Eds.), *Molten salts and ionic liquids: Never the twain?*, John Wiley & Sons, Inc., Hoboken, NJ, 2010, pp. 1–24
17. K. Kubota, K. Tamaki, T. Nohira, T. Goto, R. Hagiwara, *Electrochim. Acta* **55** (2010) 1113
18. 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: H. Ohno (Ed.), *Electrochemical aspects of ionic liquids*, John Wiley & Sons, Inc., Hoboken, NJ, 2011, pp. 5–33
19. M. V. Šušić, S. V. Mentus, *J. Chem. Phys.* **62** (1975) 744
20. H. Wang, Y. Jia, X. Wang, J. Ma, Y. Jing, *J. Chil. Chem. Soc.* **57** (2012) 1208
21. V. M. Parikh, *Absorption spectroscopy of organic molecules*, Addison-Wesley Publishing Company, London, 1974, p. 258
22. D. Z. Troter, M. Z. Zlatković, B. S. Đorđević, D. R. Đokić-Stojanović, S. S. Konstantinović, Z. B. Todorović, V. B. Veljković, in *Proceeding of 13th International Conference on Fundamental and Applied Aspects of Physical Chemistry*, (2016), Belgrade, Serbia, Society of Physical Chemists of Serbia, Belgrade, 2006, pp. 159–162
23. N. R. Rao, R. Venkataraghavan, *Spectrochim. Acta* **18** (1962) 541.