SUPPLEMENTARY MATERIAL TO

The physico-chemical and thermodynamic properties of the choline chloride-based deep eutectic solvents

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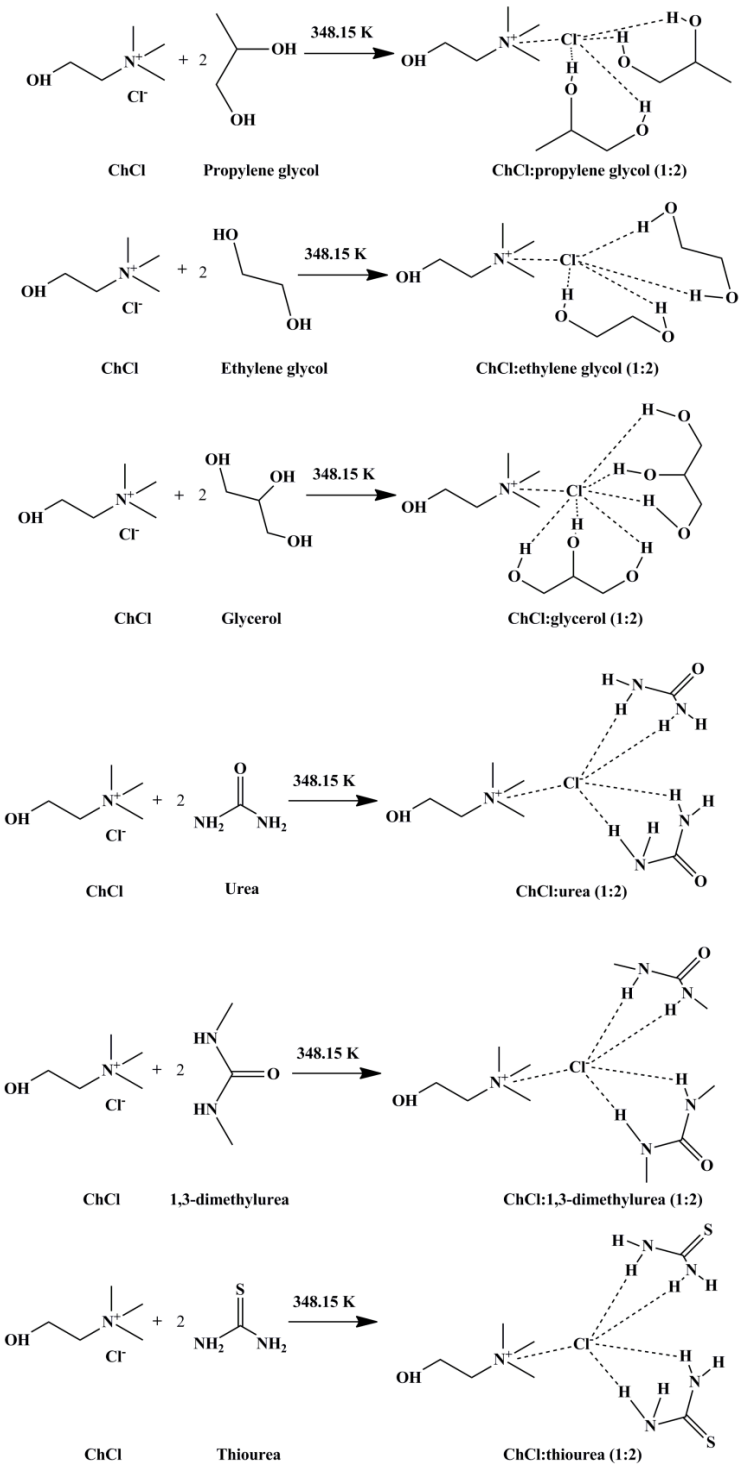

Fig. S-I. Schematic presentation of the ChCl-based DESs preparation.

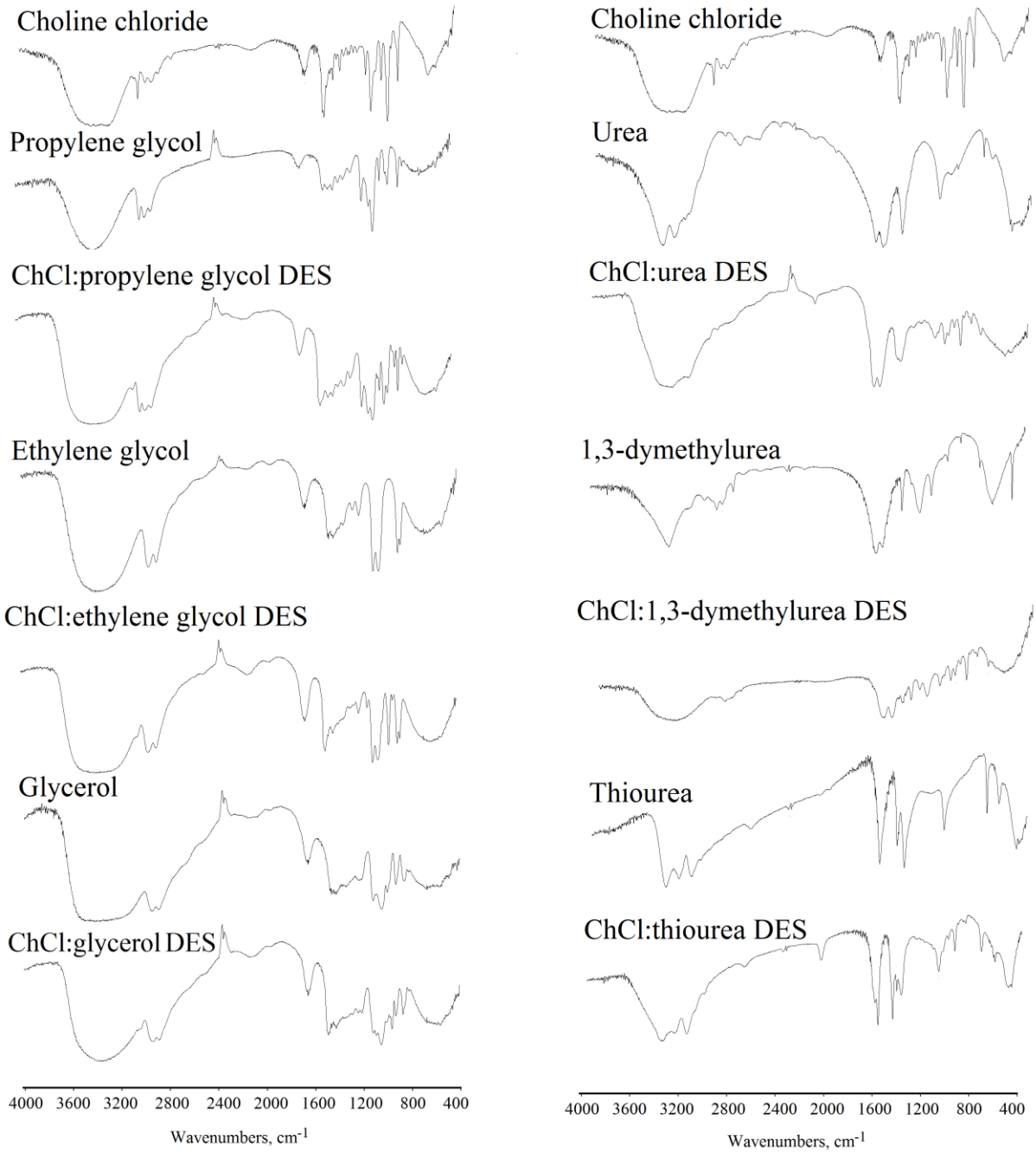

Fig. S-2. FTIR spectra of ChCl, propylene glycol, ChCl:propylene glycol DES, ethylene glycol, ChCl:ethylene glycol DES, glycerol, ChCl:glycerol DES, urea, ChCl:urea DES, 1,3-dimethylurea, ChCl:1,3-dimethylurea DES, thiourea and ChCl:thiourea DES.

(FTIR spectra discussion: The spectra of ChCl has very strong and broad band at 3406 cm^{-1}, which belongs to ν(OH) stretching vibration. The shape of 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 cm^{-1} also confirms existence of hydrogen bonds.[53] The band at 3247 cm^{-1} belongs to ν(NH_3^+) vibrations, typical for charged amine derivatives, while appropriate deformation vibration δ(NH_3^+) appears at 1660 cm^{-1}.[54]

The FTIR spectra of ChCl-based DESs with propylene glycol, ethylene glycol and glycerol show a strong and broad band at ~3400 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 shows a strong and broad band at ~3400 cm^{-1} which, as in ChCl spectra, belongs to hydrogen bonded hydroxyl functional group. The DES of ChCl and urea possesses band of charged amine derivatives slightly moved at 3334 and 3205 cm^{-1}, which is expected, considering its suggested structure. On the other hand, the spectrum of DES does not have a vibration at 1684 cm^{-1}, which can be found in the spectra of urea. This position is characteristic for carbonyl ν(C=O) vibration, suggesting the enol tautomeric form of urea in this DES. As reported elsewhere[55] the spectra of ChCl DESs with thiourea and 1,3-dimethylurea also has a strong and broad band at ~3400 cm^{-1} which, as in ChCl spectra, belongs to hydrogen bonded hydroxyl functional group. FTIR spectrum of 1,3-dimethylurea has a stretching vibration at 3345 cm^{-1}, which corresponds to secondary ν(NH) group. Bands at 2344 cm^{-1} and 1837 cm^{-1} come from stretching ν($C=NH^+$) and deformation δ($C=NH^+$) vibrations, which confirms that the 1,3-dimethylurea is in its imidic acid form ((*Z*)-*N*,*N*`-dimethylcarbamimidic acid). The band belonging to stretching ν(OH) vibration is widely broad at 3378 cm^{-1} and covers all the amine vibrations' belonging bands. ν(C-O) vibration in DES is slightly moved for $\Delta\nu$ = 11 cm^{-1} in DES's spectrum, mostly because of choline-1,3-dimethylurea interaction. FTIR spectrum of thiourea possess asymmetrical and symmetrical stretching vibrations $\nu_{as}(NH_2)$ + $\nu_s(NH_2)$ at 3380 and 3273 cm^{-1}, as well as N-C=S I, N-C=S II and N-C=S III bands at 1436, 1399 and 1084 cm^{-1}, proving that thiourea is in its thiol form (carbamimidothioic acid).[56] The slightly shift of amine deformational vibrations ($\Delta\nu$ = 11 cm^{-1}) is also explained by choline-thiourea interaction).

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

DES	Density range / kgm^{-3}	*a* / kgm^{-3}	*b* / $kgm^{-3}K^{-1}$	*MRPD* / %	R^2
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[a]	1061.2-1362.6	3168.0	- 5.7929	±0.60	0.990
ChCl:thiourea[b]	1170.9-1361.3	2409.4	- 3.4017	±0.29	0.993

[a]313.15-363.15 K;[b]308.15-363.15 K

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

DES	c / kgm^{-3}K^{-1}	α / K^{-1}	*MRPD* / %	R^2
ChCl:propylene glycol	7.2023	$4 \cdot 10^{-4}$	±0.05	0.993
ChCl:ethylene glycol	7.1810	$6 \cdot 10^{-4}$	±0.09	0.997
ChCl:glycerol	7.2629	$6 \cdot 10^{-4}$	±0.02	0.990
ChCl:urea	7.1493	$3 \cdot 10^{-4}$	±0.21	0.985
ChCl:1,3-dimethylurea[a]	8.7166	$48 \cdot 10^{-4}$	±0.09	0.991
ChCl:thiourea[b]	8.0453	$27 \cdot 10^{-4}$	±0.06	0.991

[a]313.15-363.15 K;[b]308.15-363.15 K

TABLE III. The calculated values of V_m, U_{pot} and C_p for the prepared DESs at 303.15 K

DES	V_m / nm^3	U_{pot} / kJmol^{-1}	C_p / Jmol^{-1}
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[a]	0.385	1184.7	444.1
ChCl:thiourea[b]	0.356	1220.6	414.2

[a]313.15 K;[b]308.15 K

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

DES	Viscosity range / Pas	Viscosity Arrhenius Equations (η / Pas)	A_η / Pas	E_η / Jmol^{-1}	*MRPD* / %	R^2
ChCl:propylene glycol	0.021-0.159	$\ln \eta = 2984.7 \cdot (T^{-1}) - 12.2$	$5.14 \cdot 10^{-6}$	24815	±3.45	0.966
ChCl:ethylene glycol	0.007-0.059	$\ln \eta = 2736.8 \cdot (T^{-1}) - 12.2$	$5.23 \cdot 10^{-6}$	22754	±2.10	0.963
ChCl:glycerol	0.008-0.490	$\ln \eta = 6376.3 \cdot (T^{-1}) - 22.3$	$2.16 \cdot 10^{-10}$	53013	±8.13	0.983
ChCl:urea	0.018-3.195	$\ln \eta = 8987.6 \cdot (T^{-1}) - 29.0$	$2.58 \cdot 10^{-13}$	74723	±19.72	0.968

ChCl:1,3-dimethylurea[a]	0.029-4.029	$\ln \eta = 11489\cdot(T^{-1}) - 35.5$	$4.01\cdot10^{-16}$	95519.5	±15.82	0.991
ChCl:thiourea[b]	0.094-2.972	$\ln \eta = 6971.9\cdot(T^{-1}) - 21.7$	$3.88\cdot10^{-10}$	57964.4	±14.44	0.984

[a]313.15-363.15 K;[b]308.15-363.15 K

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

DES	VTF equation	η_0 / Pas	B_η / K	T_0 / K	*MRPD* / %	R^2
ChCl:propylene glycol	$\ln \eta = 252.03\cdot(T-T_0)^{-1} - 5.7$	$3.348\cdot10^{-3}$	252.03	228	±1.61	0.990
ChCl:ethylene glycol	$\ln \eta = 2636.3\cdot(T-T_0)^{-1} - 12.01$	$6.107\cdot10^{-6}$	2636.3	6	±2.10	0.964
ChCl:glycerol	$\ln \eta = 5393\cdot(T-T_0)^{-1} - 20.68$	$1.044\cdot10^{-9}$	5393.0	26	±8.42	0.983
ChCl:urea	$\ln \eta = 7400.3\cdot(T-T_0)^{-1} - 26.43$	$3.32\cdot10^{-12}$	7400.3	30	±20.16	0.968
ChCl:1,3-dimethylurea[a]	$\ln \eta = 4578.7\cdot(T-T_0)^{-1} - 22.91$	$1.127\cdot10^{-10}$	4578.7	124	±9.57	0.995
ChCl:thiourea[b]	$\ln \eta = 2819.4\cdot(T-T_0)^{-1} - 14.07$	$7.753\cdot10^{-7}$	2819.4	121	±18.73	0.984

[a]313.15-363.15 K;[b]308.15-363.15 K

TABLE VI. The thermodynamic functions of activation of viscous flow, as well as the values of ΔH^*, ΔS^* and ΔG^* at 313.15 K, for the tested DESs

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

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

DES	Conductivity range / Sm^{-1}	Conductivity Arrhenius equations (κ /Sm^{-1})	A_κ / Sm^{-1}	E_κ / Jmol^{-1}	*MRPD* / %	R^2

ChCl:propylene glycol	2.860-10.870	$ln\,\kappa = -1948.6 \cdot T^{-1} + 7.8$	2584	16200	±4.72	0.957
ChCl:ethylene glycol	8.260-21.550	$ln\,\kappa = -1391.4 \cdot T^{-1} + 6.9$	1012	11568	±0.95	0.989
ChCl:glycerol	1.088-11.227	$ln\,\kappa = -3590.8 \cdot T^{-1} + 12.3$	220356	29853	±7.50	0.995
ChCl:urea	0.369-8.220	$ln\,\kappa = -4574.1 \cdot T^{-1} + 14.8$	2808047	38029	±13.68	0.976
ChCl:1,3-dimethylurea[a]	0.264-1.119	$ln\,\kappa = -3307.8 \cdot T^{-1} + 9.2$	10055.7	27501	±3.13	0.998
ChCl:thiourea[b]	1.204-3.612	$ln\,\kappa = -2240.5 \cdot T^{-1} + 7.4$	1718.1	18627.5	±1.83	0.999

[a]313.15-363.15 K;[b]308.15-363.15 K

TABLE VIII. VTF equation parameters of conductivity

DES	VTF equation	κ_0 / Sm^{-1}	B_κ / K	T_0 / K	*MRPD* / %	R^2
ChCl:propylene glycol	$ln\,\kappa = -98.52 \cdot (T-T_0)^{-1} + 3.2381$	25.5	98.52	248.1	±0.34	0.999
ChCl:ethylene glycol	$ln\,\kappa = -196.76 \cdot (T-T_0)^{-1} + 4.2603$	70.83	196.76	201.0	±0.75	0.994
ChCl:glycerol	$ln\,\kappa = -3375.5 \cdot (T-T_0)^{-1} + 11.968$	157629.1	3375.5	9.9	±7.81	0.995
ChCl:urea	$ln\,\kappa = -601.12 \cdot (T-T_0)^{-1} + 5.9321$	376.9	601.12	205.7	±4.27	0.996
ChCl:1,3-dimethylurea[a]	$ln\,\kappa = -527.38 \cdot (T-T_0)^{-1} + 3.3153$	27.5	527.38	201.0	±11.63	0.992
ChCl:thiourea[b]	$ln\,\kappa = -1086.9 \cdot (T-T_0)^{-1} + 5.4118$	224.03	1086.9	100.8	±3.07	0.998

[a]313.15-363.15 K;[b]308.15-363.15 K

TABLE IX. VTF equation parameters of molar conductivity

DES	VTF equation	Λ_0 / Sm^2mol^{-1}	B_Λ / K	T_0 / K	*MRPD* / %	R^2
ChCl:propylene glycol	$ln\,\Lambda = -94.693 \cdot (T-T_0)^{-1} - 5.074$	0.0063	94.693	250	±0.13	0.999
ChCl:ethylene glycol	$ln\,\Lambda = -280.42 \cdot (T-T_0)^{-1} - 3.710$	0.0245	280.42	181	±0.31	0.995
ChCl:glycerol	$ln\,\Lambda = -3218.4 \cdot (T-T_0)^{-1} + 3.617$	37.237	3218.4	20	±0.52	0.995
ChCl:urea	$ln\,\Lambda = -370.84 \cdot (T-T_0)^{-1} - 3.567$	0.0282	370.84	230	±0.59	0.998
ChCl:1,3-dimethylurea[a]	$ln\,\Lambda = -3408.2 \cdot (T-T_0)^{-1} + 1.905$	6.7212	3408.2	20	±0.16	0.999
ChCl:thiourea[b]	$ln\,\Lambda = -2243.1 \cdot (T-T_0)^{-1} - 0.491$	0.6122	2243.1	20	±0.17	0.999

[a]313.15-363.15 K;[b]308.15-363.15 K

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

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

[a]$log\ \Lambda = 0.6654 \cdot log\ \eta^{-1} - 3.6612$; [b]$log\ \Lambda = 0.5121 \cdot log\ \eta^{-1} - 3.3006$; [c]$log\ \Lambda = 0.5681 \cdot log\ \eta^{-1} - 3.6631$; [d]$log\ \Lambda = 0.4891 \cdot log\ \eta^{-1} - 3.5997$; [e]$log\ \Lambda = 0.3318 \cdot log\ \eta^{-1} - 4.0384$ and [f]$log\ \Lambda = 0.3584 \cdot log\ \eta^{-1} - 3.4401$

TABLE 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[a]	1.493-1.507	1.566	- 0.0002	±2.67	0.997
ChCl:1,3-dimethylurea[a]	1.469-1.480	1.5338	- 0.0002	±0.46	0.977
ChCl:thiourea[b]	1.509-1.525	1.6019	- 0.0003	±0.89	0.974

[a]Temperature range: 303.15-363.15 K, [*]298.15-363.15 K

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

DES	υ / $ms^{-1} \cdot 10^7$	A / $m^3mol^{-1} \cdot 10^{-6}$
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[a]	20.26-20.41[a]	65.64-83.00[b]
ChCl:thiourea[b]	19.66-19.87[a]	66.11-74.45[b]

[a]298.15-363.15 K, [b]313.15-363.15 K