SUPPLEMENTARY MATERIAL

**The physicochemical and thermodynamic properties of the deep eutectic solvents with triethanolamine**

BILJANA S. ĐORĐEVIĆ1, DRAGAN Z. TROTER1, VLADA B. VELJKOVIĆ1,2, MIRJANA LJ. KIJEVČANIN3, IVONA R. RADOVIĆ3 and ZORAN B. TODOROVIĆ1[[1]](#footnote-1)\*

*1University of Niš, Faculty of Technology, Bulevar Oslobođenja 124, 16000 Leskovac, Serbia*

*2Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia*

*3Faculty of**Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*

TABLE S-I. Information on the used chemicals

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Chemical name | Abbreviation | Formula | Molar mass / g·mol-1 | Chemical structure | CAS number |
| Triethanolamine | TEOA | C6H15NO3 | 149.19 |  | 102-71-6 |
| Oxalic acid | OA | C2H2O4 | 90.03 |  | 144-62-7 |
| Glacial acetic acid | AA | C2H4O2 | 60.05 |  | 64-19-7 |
| L-(+)-Lactic acid | LA | C3H6O3 | 90.08 |  | 50-21-5 |
| Oleic acid | OLA | C18H34O2 | 282.47 |  | 112-80-1 |
| Glycerol | G | C3H8O3 | 92.09 |  | 56-81-5 |
| Ethylene glycol | EG | C2H6O2 | 62.07 |  | 107-21-1 |
| Propylene glycol | PEG | C3H8O2 | 76.09 |  | 57-55-6 |
| Choline chloride | ChCl | C5H14ClNO | 139.62 |  | 67-48-1 |
| 1,3-Dimethylurea | DMU | C3H8N2O | 88.11 |  | 96-31-1 |

TABLE S-II.Prepared DESsa

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| DES | Abbreviation | Molar ratio / mol:mol | Molar mass of DES \* / g·mol-1 | Water content (mass fraction) |
| Triethanolamine:oxalic acid | TEOA:OA | 1:1 | 119.61 | 0.0007 |
| Triethanolamine:acetic acid | TEOA:AA | 1:1 | 104.62 | 0.0006 |
| Triethanolamine: L-(+)-lactic acid | TEOA:LA | 1:1 | 119.64 | 0.0004 |
| Triethanolamine:oleic acid | TEOA:OLA | 1:1 | 215.83 | 0.0007 |
| Triethanolamine:glycerol | TEOA:G | 1:2 | 110.93 | 0.0006 |
| Triethanolamine:ethylene glycol | TEOA:EG | 1:2 | 90.82 | 0.0005 |
| Triethanolamine:propylene glycol | TEOA:PEG | 1:2 | 100.21 | 0.0004 |
| Choline chloride: triethanolamine | ChCl:TEOA | 1:2 | 146.03 | 0.0006 |
| Triethanolamine:1,3-dimethylurea | TEOA:DMU | 1:2 | 108.27 | 0.0004 |

a HBA – as hydrogen bond acceptor, HBD – hydrogen bond donor. The of molecular mass (*M*DES) for TEOA-based DESs is determined from Eq1: , where *M*DES is the molecular mass of DES in g·mol−1, *x*HBA and *M*HBA are the mole ratio and molecular mass of the HBA in g·mol−1, respectively; *x*HBD and *M*HBD are the mole ratio and molecular mass of the HBD in g·mol−1, in order.

TABLE S-III. The physicochemical properties of TEOA:OA DESa

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *T*/ K | *ρ* / kg∙m-3 | *η /* Pa∙s | *κ* / S∙m-1 | *n*D |
| 293.15 | 1362.2 | 0.7261 | 0.102 | 1.48016 |
| 303.15 | 1357.9 | 0.4869 | 0.120 | 1.47717 |
| 313.15 | 1350.8 | 0.2386 | 0.162 | 1.47391 |
| 323.15 | 1346.4 | 0.1088 | 0.251 | 1.47118 |
| 333.15 | 1342.4 | 0.0701 | 0.340 | 1.46816 |
| 343.15 | 1338.5 | 0.0441 | 0.467 | 1.46450 |
| 353.15 | 1334.7 | 0.0377 | 0.503 | 1.46219 |
| 363.15 | 1330.8 | 0.0363 | 0.564 | 1.45918 |

a Uncertainties (u): (u)*T* = ±0.005 K; (u)*ρ* = ±0.5 kg∙m–3; (u) *η* = 5% of the measured value; (u)*k* = ± 0.0001 S∙m–1; (u)*n*D = ±0.00005.

TABLE S-IV. The physicochemical properties of TEOA:AA DESa

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *T* / K | *ρ* / kg∙m-3 | *η /* Pa∙s | *κ* / S∙m-1 | *n*D |
| 293.15 | 1182.9 | 1.2054 | 0.0189 | 1.47778 |
| 303.15 | 1181.7 | 0.8143 | 0.0202 | 1.47585 |
| 313.15 | 1179.4 | 0.4114 | 0.029 | 1.47365 |
| 323.15 | 1176.6 | 0.1944 | 0.046 | 1.47171 |
| 333.15 | 1174.8 | 0.0991 | 0.086 | 1.46978 |
| 343.15 | 1173 | 0.0651 | 0.111 | 1.46769 |
| 353.15 | 1171.3 | 0.0534 | 0.159 | 1.46574 |
| 363.15 | 1168.9 | 0.0511 | 0.22 | 1.46385 |

a Uncertainties (u): (u)*T* = ±0.005 K; (u)*ρ* = ±0.5 kg∙m–3; (u) *η* = 5% of the measured value; (u)*k* = ± 0.0001 S∙m–1; (u)*n*D = ±0.00005.

TABLE S-V. The physicochemical properties of TEOA:LA DESa

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *T* / K | *ρ* / kg∙m-3 | *η /* Pa∙s | *κ* / S∙m-1 | *n*D |
| 293.15 | 1265.4 | 1.7377 | 0.004 | 1.47999 |
| 303.15 | 1258.2 | 1.218 | 0.019 | 1.47874 |
| 313.15 | 1252.3 | 0.7572 | 0.026 | 1.47782 |
| 323.15 | 1244.6 | 0.2714 | 0.052 | 1.47647 |
| 333.15 | 1238.9 | 0.1922 | 0.095 | 1.47574 |
| 343.15 | 1230.2 | 0.1102 | 0.199 | 1.47482 |
| 353.15 | 1224.1 | 0.0406 | 0.356 | 1.47363 |
| 363.15 | 1216.9 | 0.0094 | 0.598 | 1.47291 |

a Uncertainties (u): (u)*T* = ±0.005 K; (u)*ρ* = ±0.5 kg∙m–3; (u) *η* = 5% of the measured value; (u)*k* = ± 0.0001 S∙m–1; (u)*n*D = ±0.00005.

TABLE S-VI. The physicochemical properties of TEOA:OLA DESa

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *T* / K | *ρ* / kg∙m-3 | *η /* Pa∙s | *κ* / S∙m-1 | *n*D |
| 293.15 | 1114.9 | 39.76 | 0.00555 | 1.43984 |
| 303.15 | 1108.9 | 25.93 | 0.00682 | 1.43789 |
| 313.15 | 1102.9 | 12.64 | 0.0127 | 1.43372 |
| 323.15 | 1096.9 | 4.542 | 0.0327 | 1.42765 |
| 333.15 | 1090.9 | 0.1359 | 0.072 | 1.42499 |
| 343.15 | 1084.9 | 0.0949 | 0.121 | 1.41992 |
| 353.15 | 1080.1 | 0.0097 | 0.159 | 1.41785 |
| 363.15 | 1077.9 | 0.0046 | 0.1812 | 1.41374 |

a Uncertainties (u): (u)*T* = ±0.005 K; (u)*ρ* = ±0.5 kg∙m–3; (u) *η* = 5% of the measured value; (u)*k* = ± 0.0001 S∙m–1; (u)*n*D = ±0.00005.

TABLE S-VII. The physicochemical properties of TEOA:G DESa

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *T* / K | *ρ* / kg∙m-3 | *η /* Pa∙s | *κ* / S∙m-1 | *n*D |
| 293.15 | 1249.2 | 0.3124 | 0.00056 | 1.46873 |
| 303.15 | 1242.7 | 0.1749 | 0.00089 | 1.46735 |
| 313.15 | 1234.4 | 0.0948 | 0.0013 | 1.46645 |
| 323.15 | 1230.9 | 0.0355 | 0.00251 | 1.46528 |
| 333.15 | 1224.2 | 0.0082 | 0.00446 | 1.46472 |
| 343.15 | 1218.7 | 0.0028 | 0.00667 | 1.46385 |
| 353.15 | 1212.5 | 0.0019 | 0.00824 | 1.46254 |
| 363.15 | 1206.7 | 0.0011 | 0.00945 | 1.46129 |

a Uncertainties (u): (u)*T* = ±0.005 K; (u)*ρ* = ±0.5 kg∙m–3; (u) *η* = 5% of the measured value; (u)*k* = ± 0.0001 S∙m–1; (u)*n*D = ±0.00005.

TABLE S-VIII. The physicochemical properties of TEOA:EG DES.a

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *T* / K | *ρ* / kg∙m-3 | *η /* Pa∙s | *κ* / S∙m-1 | *n*D |
| 293.15 | 1147.2 | 0.0795 | 0.00332 | 1.45585 |
| 303.15 | 1139.7 | 0.0542 | 0.00481 | 1.45536 |
| 313.15 | 1132.8 | 0.0369 | 0.00674 | 1.45472 |
| 323.15 | 1126.9 | 0.0238 | 0.00753 | 1.45421 |
| 333.15 | 1119.5 | 0.0112 | 0.00998 | 1.45387 |
| 343.15 | 1117.3 | 0.0056 | 0.01126 | 1.45325 |
| 353.15 | 1111.7 | 0.0025 | 0.01254 | 1.45282 |
| 363.15 | 1104.7 | 0.0008 | 0.01485 | 1.45234 |

a Uncertainties (u): (u)*T* = ±0.005 K; (u)*ρ* = ±0.5 kg∙m–3; (u) *η* = 5% of the measured value; (u)*k* = ± 0.0001 S∙m–1; (u)*n*D = ±0.00005.

TABLE S-IX. The physicochemical properties of TEOA:PG DESa

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *T* / K | *ρ* / kg∙m-3 | *η /* Pa∙s | *κ* / S∙m-1 | *n*D |
| 293.15 | 1092.2 | 0.1027 | 0.00015 | 1.44928 |
| 303.15 | 1081.4 | 0.0657 | 0.0004 | 1.44869 |
| 313.15 | 1073.2 | 0.0386 | 0.00085 | 1.44788 |
| 323.15 | 1069.1 | 0.0138 | 0.00184 | 1.44599 |
| 333.15 | 1062.1 | 0.0086 | 0.00247 | 1.44501 |
| 343.15 | 1056.9 | 0.0048 | 0.00281 | 1.44422 |
| 353.15 | 1048.5 | 0.0023 | 0.0034 | 1.44356 |
| 363.15 | 1042.1 | 0.001 | 0.00699 | 1.44281 |

a Uncertainties (u): (u)*T* = ±0.005 K; (u)*ρ* = ±0.5 kg∙m–3; (u) *η* = 5% of the measured value; (u)*k* = ± 0.0001 S∙m–1; (u)*n*D = ±0.00005.

TABLE S-X. The physicochemical properties of TEOA:ChCl DESa

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *T* / K | *ρ* / kg∙m-3 | *η /* Pa∙s | *κ* / S∙m-1 | *n*D |
| 293.15 | 1178.9 | 1.881 | 0.2196 | 1.4814 |
| 303.15 | 1173.8 | 0.704 | 0.301 | 1.4803 |
| 313.15 | 1168.6 | 0.501 | 0.5375 | 1.4789 |
| 323.15 | 1163.7 | 0.319 | 0.75 | 1.4781 |
| 333.15 | 1158.4 | 0.1742 | 1.56 | 1.4773 |
| 343.15 | 1153.3 | 0.0386 | 2.215 | 1.4764 |
| 353.15 | 1148.9 | 0.0272 | 4.773 | 1.4755 |
| 363.15 | 1145.2 | 0.0189 | 9.003 | 1.4743 |

a Uncertainties (u): (u)*T* = ±0.005 K; (u)*ρ* = ±0.5 kg∙m–3; (u) *η* = 5% of the measured value; (u)*k* = ± 0.0001 S∙m–1; (u)*n*D = ±0.00005.

TABLE S-XI. The physicochemical properties of TEOA:DMU DESa

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *T* / K | *ρ* / kg∙m-3 | *η /* Pa∙s | *κ* / S∙m-1 | *n*D |
| 293.15 | 1182.6 | 7.244 | 0.0018 | 1.4991 |
| 303.15 | 1173.4 | 2.623 | 0.0029 | 1.494 |
| 313.15 | 1163.7 | 1.1921 | 0.0041 | 1.4886 |
| 323.15 | 1153.2 | 0.3502 | 0.0093 | 1.4839 |
| 333.15 | 1143.3 | 0.0952 | 0.0197 | 1.478 |
| 343.15 | 1129.1 | 0.0232 | 0.0319 | 1.4745 |
| 353.15 | 1116.9 | 0.00677 | 0.0405 | 1.4687 |
| 363.15 | 1113.2 | 0.00289 | 0.0447 | 1.4642 |

a Uncertainties (u): (u)*T* = ±0.005 K; (u)*ρ* = ±0.5 kg∙m–3; (u) *η* = 5% of the measured value; (u)*k* = ± 0.0001 S∙m–1; (u)*n*D = ±0.00005.

*Effect of temperature on density of DESs*

The density of the tested DESs slightly decreases linearly which agrees with the previous reports.2,3-5 The density-temperature correlation can be outlined by a linear equation (1):

*ρ = a + b·T* (1)

where *ρ*, *T*, *a* and *b* represent the density, the absolute temperature, the density at 0 K and the coefficient of volume expansion, respectively. The characteristic parameters *a* and *b* of Eq. (1), density ranges, mean relative percent deviation (*MRPD*) and the coefficient of determination (*R*2) are given in Table S-XII. A good linear dependence of density on temperature is confirmed by the low *MRPD*-values (<0.2%) and the *R*2-values close to unity (>0.990).

TABLE S-XII.Parameters of Eq. (1) (293.15-363.15) K

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| DES | Density range / kg·m-3 | *a* /  kg·m-3 | *b* /  kg·m-3·K-1 | *MRPD* / % | *R*2 |
| TEOA:OA (1:1) | 1362.2-1330.8 | 1492.6 | -0.4485 | 0.07 | 0.990 |
| TEOA:AA (1:1) | 1182.9-1168.9 | 1242.9 | -0.2036 | 0.08 | 0.995 |
| TEOA:LA (1:1) | 1265.4-1216.9 | 1468.7 | -0.6929 | 0.04 | 0.999 |
| TEOA:OLA (1:1) | 1114.9-1077.9 | 1275.5 | -0.5512 | 0.09 | 0.991 |
| TEOA:G (1:2) | 1249.2-1206.7 | 1423.6 | -0.5980 | 0.05 | 0.997 |
| TEOA:EG (1:2) | 1147.2-1104.7 | 1316.9 | -0.5850 | 0.10 | 0.990 |
| TEOA:PEG (1:2) | 1092.2-1042.1 | 1288.8 | -0.6799 | 0.10 | 0.991 |
| ChCl:TEOA (1:2) | 1178.9-1145.2 | 1322.1 | -0.4900 | 0.03 | 0.998 |
| TEOA:DMU (1:2) | 1182.6-1113.2 | 1491.5 | -1.0500 | 0.15 | 0.993 |

Considering the values of the coefficient of volume expansion, the thermal sensitivity of these DESs is in the following order: TEOA:DMU ˃ TEOA:LA ˃ TEOA:PEG ˃ TEOA:G ˃ TEOA:EG ˃ TEOA:OLA ˃ ChCl:TEOA ˃ TEOA:OA ˃ TEOA:AA.

The molecular volume (*V*m), the lattice energy (*U*pot) and the heat capacity (*C*p) were calculated by the means of Eq. (2), (3), (4), (5) and (6)2,6 and the values obtained at 313.15 K are listed in Table S-XIII.

** (2)

where *M*DES is the molecular mass of DES in g·mol−1 and *N*A is Avogadro’s constant.

** (3)

for TEOA:OA (1:1), TEOA:AA (1:1), TEOA:LA (1:1) and TEOA:OLA (1:1).

** (4)

for TEOA:G (1:2), TEOA:EG (1:2), TEOA:PEG (1:2) and TEOA:DMU (1:2).

** (5)

for ChCl:TEOA (1:2).

*C*p = 1037*·V*m + 45 (6)

TABLE S-XIII. The values of molecular volume(*V*m), lattice energy(*U*pot) and heat capacity(*C*p)for the tested DESs at 313.15 K

|  |  |  |  |
| --- | --- | --- | --- |
| DES | *V*m / nm3 | *U*pot / kJ·mol-1 | *C*p / J·mol-1K-1 |
| TEOA:OA (1:1) | 0.147 | 548 | 197 |
| TEOA:AA (1:1) | 0.147 | 548 | 198 |
| TEOA:LA (1:1) | 0.159 | 537 | 209 |
| TEOA:OLA (1:1) | 0.325 | 445 | 382 |
| TEOA:G (1:2) | 0.149 | 1691 | 200 |
| TEOA:EG (1:2) | 0.133 | 1764 | 183 |
| TEOA:PEG (1:2) | 0.155 | 1667 | 206 |
| ChCl:TEOA (1:2) | 0.208 | 1718 | 260 |
| TEOA:DMU (1:2) | 0.154 | 1670 | 205 |

*Effect of temperature on viscosity of DESs*

The viscosity-temperature relationship of the analyzed DESs can be described by the Vogel-Tamman-Fulcher (VTF) equation is more appropriate:7

**  (7)

where *T*, *η0*, *Bη*, and *T*0 represent the absolute temperature, the adjustable parameter, the factor related to the activation energy and the so-called ideal glass-transition temperature, respectively. The values of these parameters, along with VTF equations, *MRPD* and *R*2 are shown in Table S-XIV.

TABLE S-XIV.The parameters of the VTF equation, Eq. (7), for the tested DESs (293.15-363.15) K

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| DES | Viscosity range (*η* / Pa·s) | VTF equation | | *η*0 / Pa·s | *Bη* / K | *T*0 / K | *MRPD* / % | *R*2 |
| TEOA:OA (1:1) | 0.726-0.036 | ln *η* = 645.38·(T-T0)-1- 7.664 | 4.696·10-4 | | 645.4 | 207 | 13.97 | 0.979 |
| TEOA:AA (1:1) | 1.205-0.051 | ln *η* = 995.25·(T-T0)-1- 8.773 | 1.548·10-4 | | 995.3 | 184 | 29.61 | 0.977 |
| TEOA:LA (1:1) | 1.738-0.009 | ln *η* = 7161.3·(T-T0)-1- 23.983 | 3.840·10-11 | | 7161.3 | 7 | 33.53 | 0.940 |
| TEOA:OLA (1:1) | 39.76-0.005 | ln *η* = 15048·(T-T0)-1- 46.791 | 4.774·10-21 | | 15048 | 9 | 29.39 | 0.940 |
| TEOA:G (1:2) | 0.312-0.001 | ln *η* = 9343.1·(T-T0)-1- 32.746 | 6.006·10-15 | | 9343.1 | 5 | 10.57 | 0.977 |
| TEOA:EG (1:2) | 0.080-0.001 | ln *η* = 6716.9·(T-T0)-1- 25.044 | 1.329·10-11 | | 6716.9 | 8 | 7.80 | 0.941 |
| TEOA:PEG (1:2) | 0.103-0.001 | ln *η* = 7019.1·(T-T0)-1- 26.013 | 5.043·10-12 | | 7019.1 | 11 | 4.29 | 0.985 |
| ChCl:TEOA (1:2) | 1.881-0.019 | ln *η* = 7134·(T-T0)-1- 23.681 | 5.194·10-11 | | 7134 | 10 | 24.41 | 0.965 |
| TEOA:DMU (1:2) | 7.244-0.003 | ln *η* = 12191·(T-T0)-1- 39.425 | 7.550·10-18 | | 12191 | 12 | 41.71 | 0.987 |

TABLE S-XV.The thermodynamic functions of activation of viscous flow, Δ*H\**, Δ*S\** and Δ*G\*,* and *R*2 for the tested DESs at 313.15 K

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| DES | Eyring’s equation | *R*2 | Δ*H*\*/ kJ·mol-1 | *T*Δ*S*\*/ kJ·mol-1 | Δ*G*\*/ kJ·mol-1 |
| TEOA:OA (1:1) | ln (*ηV*/h*N*A) = 5003·T-1 – 5.143 | 0.960 | 41.59 | 13.34 | 28.20 |
| TEOA:AA (1:1) | ln (*ηV*/h*N*A) = 5355.9·T-1 - 5.774 | 0.962 | 44.52 | 15.03 | 29.49 |
| TEOA:LA (1:1) | ln (*ηV*/h*N*A) = 7427.1·T-1 - 11.921 | 0.930 | 61.75 | 31.04 | 30.71 |
| TEOA:OLA (1:1) | ln (*ηV*/h*N*A) = 15191.3·T-1 - 33.835 | 0.930 | 126.30 | 88.09 | 38.21 |
| TEOA:G (1:2) | ln ((*ηV*/h*N*A) = 9354.9·T-1 – 20.364 | 0.972 | 77.78 | 53.02 | 24.76 |
| TEOA:EG (1:2) | ln ((*ηV*/h*N*A) = 6707.3·T-1 – 12.734 | 0.930 | 55.76 | 33.15 | 22.61 |
| TEOA:PEG (1:2) | ln (*ηV*/h*N*A) = 6998.3·T-1 – 13.514 | 0.982 | 58.18 | 35.18 | 22.99 |
| ChCl:TEOA (1:2) | ln (*ηV*/h*N*A) = 7138.1·T-1 – 10.965 | 0.960 | 59.34 | 28.55 | 30.80 |
| TEOA:DMU (1:2) | ln (*ηV*/h*N*A) = 12252.8·T-1 – 27.011 | 0.985 | 101.87 | 70.32 | 31.54 |

The values of the molar enthalpy change of activation for the viscous flow are higher than the *T*Δ*S*\*values, implying that the energetic contribution corresponding to the molar enthalpy change of activation for the viscous flow is more important than the entropic contribution to the molar Gibbs energy change of activation.

*Effect of temperature on the electrical conductivity of DESs*

Analogous to the viscosity, the electrical conductivity-temperature relationship is also described by the VTF equation;8

** (8)

where *κ*0, *Bk* and *T*0 represent the preexponential factor, a factor correlated to the activation energy and the ideal glass-transition temperature, respectively. The fitting parameters of the VTF equation for the electrical conductivity of the tested DESs are summarized in Table S-XVI. The preexponential factor *κ*0 is correlated with the number of mobile charge carriers in the molecule. The highest *κ*0 value of ChCl:TEOA is due to its enhanced ion dissociation while the lowest *κ*0 of TEOA:PEG is explained by the formation of the polypropylene glycol that inhibits the ion mobility.

TABLE S-XVI. The parameters of the VTF equation, Eq. (7), for the electrical conductivity (*κ*) of the tested DESs (293.15-363.15) K

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| DES | VTF equation | *κ*0 / S∙m-1 | *Bκ /* K | *T*0 / K | *MRPD /* % | *R*2 |
| TEOA:OA (1:1) | ln *κ* = -1258.3·(*T*-*T*0)-1 + 4.4946 | 89.5 | 1258.3 | 110 | 7.47 | 0.979 |
| TEOA:AA (1:1) | ln *κ* = -4038.1·(*T*-*T*0)-1 + 9.5925 | 14654.50 | 4038.1 | 11 | 3.72 | 0.975 |
| TEOA:LA (1:1) | ln *κ* = -3282.3·(*T*-*T*0)-1 + 12.1660 | 192143.90 | 3282.3 | 105 | 4.31 | 0.986 |
| TEOA:OLA (1:1) | ln *κ* = -3621.5·(*T*-*T*0)-1 + 11.0850 | 65186 | 3621.5 | 74 | 7.32 | 0.969 |
| ChCl:TEOA (1:2) | ln *κ* = -5607.1·(*T*-*T*0)-1 + 17.3960 | 35891103.20 | 5607.1 | 10 | 23.5 | 0.979 |
| TEOA:DMU (1:2) | ln *κ* = -2390.9·(*T*-*T*0)-1 + 6.5285 | 684.40 | 2390.9 | 109 | 3.89 | 0.979 |
| TEOA:G (1:2) | ln *κ* = -1647.2·(*T*-*T*0)-1 + 2.5920 | 13.40 | 1647.2 | 131 | 1.82 | 0.985 |
| TEOA:EG (1:2) | ln *κ* = -219.03·(*T*-*T*0)-1 - 2.7029 | 0.08 | 219.03 | 220 | 0.58 | 0.995 |
| TEOA:PEG (1:2) | ln *κ* = -310.9·(*T*-*T*0)-1 - 2.6100 | 0.07 | 310.9 | 243 | 2.11 | 0.983 |

*Molar conductivity and viscosity relationship*

The equation used for determining the molar conductivity (*Λ*) is:

** (9)

where *κ* is the electrical conductivity*, M* is the molar mass and *ρ* is the density. The empirical VTF equation for the molar conductivity is as follows:

** (10)

where *Λ*0, *BΛ* and *T*0 are the fitting parameters. Their values are given in Table S-XVII.

TABLE S-XVII**.** The parameters of VTF equation, Eq. (10), for the molar conductivity (*Λ*) of the tested DESs over the temperature range (293.15-363.15) K

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| DES | VTF equation | *Λ*0 / S∙m2∙mol–1 | *BΛ* / K | *T*0 / K | *MRPD /* % | *R*2 |
| TEOA:OA (1:1) | ln *Λ* = -1285.8·(*T*-*T*0)-1 - 4.7336 | 0.009 | 1285.8 | 109 | 0.76 | 0.975 |
| TEOA:AA (1:1) | ln *Λ* = -4006.3·(*T*-*T*0)-1 + 0.2439 | 1.276 | 4006.3 | 3 | 0.92 | 0.970 |
| TEOA:LA (1:1) | ln *Λ* = -3339.8·(*T*-*T*0)-1 + 3.1104 | 22.430 | 3339.8 | 104 | 0.97 | 0.984 |
| TEOA:OLA (1:1) | ln *Λ* = -3566.3·(*T*-*T*0)-1 + 2.5061 | 12.257 | 3566.3 | 77 | 1.78 | 0.964 |
| TEOA:G (1:2) | ln *Λ* = -1529.2·(*T*-*T*0)-1 – 6.9835 | 0.001 | 1529.2 | 139 | 0.68 | 0.984 |
| TEOA:EG (1:2) | ln *Λ* = -233.8·(*T*-*T*0)-1 – 12.0295 | 5.97·10–6 | 233.8 | 218 | 0.20 | 0.994 |
| TEOA:PEG (1:2) | ln *Λ* = -332.5·(*T*-*T*0)-1 – 11.7204 | 8.13·10–6 | 332.5 | 241 | 0.80 | 0.981 |
| ChCl:TEOA (1:2) | ln *Λ* = -5651.7·(*T*-*T*0)-1 + 8.5519 | 5176.581 | 5651.7 | 1 | 1.93 | 0.971 |
| TEOA:DMU (1:2) | ln *Λ* = -2737.9·(*T*-*T*0)-1 – 1.8599 | 0.156 | 2737.9 | 96 | 1.19 | 0.972 |

The Walden plot is useful for illustrating the conductivity-viscosity relationship for the pure ionic liquids.9 It describes the connection between the mobility of ions and the fluidity of their surrounding medium according to the following equation:10

*Λ η* = *k*  (11)

where *Λ* is the molar conductivity, *η* is the viscosity and *k* is a temperature-dependent constant. Therefore, the Walden plot is used for classifying the ionic liquids as “good”, “poor”, “superionic”, *etc*.2 The logarithmic plot of *Λ*, representing the ion mobility, versus the fluidity *φ* (*φ* = *η*−1) is used for comparing the ions’ formation ability in non-aqueous electrolyte solutions, molten salts and ionic liquids.11 This so-called “fractional” Walden rule is written as follows:11

log *Λ*= log *C* + *α`*log *η*−1 (12)

where *C* is the Walden product, and α’ is the slope of the Walden plot line and reflects on the decoupling of the ions. The coefficients of the Walden equation for the DESs are given in Table S-XVIII.

TABLE S-XVIII.The coefficients of the Walden equation (12) along with *MRPD* and *R*2 for the tested DESs over the temperature range (293.15-363.15) K

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| DES | Walden equation | *α’* | *C* | *MRPD* / % | *R*2 |
| TEOA:OA (1:1) | log *Λ* = 0.5722·log *η*-1 – 5.1623 | 0.5722 | 6.88·10–6 | 0.51 | 0.988 |
| TEOA:AA (1:1) | log *Λ* = 0.7397·log *η*-1 - 5.8138 | 0.7397 | 1.54·10–6 | 1.32 | 0.947 |
| TEOA:LA (1:1) | log *Λ* = 0.9027·log *η*-1- 5.8043 | 0.9027 | 1.57·10–6 | 3.21 | 0.897 |
| TEOA:OLA (1:1) | log *Λ* = 0.3836·log *η*-1 – 5.2010 | 0.3836 | 6.3·10–6 | 2.43 | 0.926 |
| TEOA:G (1:2) | log *Λ* = 0.4939·log *η*-1- 7.4646 | 0.4939 | 3.43·10–8 | 0.64 | 0.982 |
| TEOA:EG (1:2) | log *Λ* = 0.304·log *η*-1- 6.7715 | 0.304 | 1.69·10–7 | 1.06 | 0.878 |
| TEOA:PEG (1:2) | log *Λ* = 0.7439·log *η*-1- 8.3162 | 0.7439 | 4.83·10–9 | 1.80 | 0.900 |
| ChCl:TEOA (1:2) | log *Λ* = 0.7694·log *η*-1- 4.4159 | 0.7694 | 3.84·10–5 | 2.46 | 0.945 |
| TEOA:DMU (1:2) | log *Λ* = 0.443·log *η*-1 – 6.3386 | 0.4430 | 4.59·10–7 | 1.44 | 0.962 |

*Effect of temperature on the refractive index of DESs*

The parameters of the linear equations,12 refractive index ranges, *MRPD* and *R*2 are listed in Table S-XIX.

TABLE S-XIX. The parameters of the refractive index (*nD*)equation for the tested DESs (293.15-363.15) K

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| DES | *n*D range | Intercept | Slope | *MRPD* / % | *R*2 |
| TEOA:OA (1:1) | 1.4802-1.4592 | 1.5684 | -0.0003 | 0.03 | 0.999 |
| TEOA:AA (1:1) | 1.4778-1.4639 | 1.5363 | -0.0002 | 0.01 | 0.999 |
| TEOA:LA (1:1) | 1.4800-1.4729 | 1.5094 | -0.0001 | 0.02 | 0.996 |
| TEOA:OLA (1:1) | 1.4398-1.4137 | 1.5547 | -0.0004 | 0.25 | 0.991 |
| TEOA:G (1:2) | 1.4687-1.4613 | 1.4980 | -0.0001 | 0.02 | 0.992 |
| TEOA:EG (1:2) | 1.4559-1.4523 | 1.4705 | -0.0001 | 0.01 | 0.997 |
| TEOA:PEG (1:2) | 1.4493-1.4428 | 1.4783 | -0.0001 | 0.03 | 0.979 |
| ChCl:TEOA (1:2) | 1.4814-1.4743 | 1.5098 | -0.0001 | 0.05 | 0.994 |
| TEOA:DMU (1:2) | 1.4991-1.4642 | 1.6451 | -0.0005 | 0.03 | 0.999 |

Table S-XXcontains the ranges of the phase velocity (*υ*), the molar refractivity (*A*) and the free volume (*f*m) for the tested DESs, calculated as recommended elsewhere.1,13

The phase velocities are similar for all tested DESs, the highest being for the TEOA:OLA (1:1) DES due to its lowest refraction index in the applied temperature range. The molar refractivity, which is a measure of the polarizability of a substance, is mostly influenced by the molecular mass while the temperature, density and refraction index show a weak effect. A minor effect of the temperature on molar refractivity has already been reported.1 The free volume increases with heating, as expected.1 Among all tested DESs, TEOA:OLA (1:1) has the highest free volume due to the longest alkyl chain of oleic acid.1

At 313.15 K, the phase velocity of the tested DESs is in following order: TEOA:DMU < ChCl:TEOA < TEOA:LA < TEOA:OA < TEOA:AA < TEOA:G < TEOA:EG < TEOA:PEG < TEOA:OLA.

TABLE S-XX. The phase velocity (*υ*), molar refractivity (*A*) and free volume (*f*m) ranges for the tested DESs (293.15-363.15) K.

|  |  |  |  |
| --- | --- | --- | --- |
| DES | *υ* / 107 m∙s-1 | *A* / 10-6 m3∙mol-1 | *f*m / 10-6 m3∙mol-1 |
| TEOA:OA (1:1) | 20.27-20.56 | 24.57-24.95 | 62.29-6289 |
| TEOA:AA (1:1) | 24.69-25.03 | 49.38-50.05 | 64.81-63.42 |
| TEOA:LA (1:1) | 20.27-20.37 | 26-85-27-57 | 67.85-70.74 |
| TEOA:OLA (1:1) | 20.84-21.22 | 50.01-51.00 | 142.58-150.22 |
| TEOA:G (1:2) | 20.43-20.53 | 24.72-25.23 | 64.08-66.69 |
| TEOA:EG (1:2) | 20.61-20.66 | 21-51-22.19 | 57.65-60.02 |
| TEOA:PEG (1:2) | 20.70-20.79 | 35.27-35.85 | 88.59-91.66 |
| ChCl:TEOA (1:2) | 20.25-20.35 | 26.84-26.88 | 64.66-70.41 |
| TEOA:DMU (1:2) | 20.01-20.49 | 32.33-35-76 | 79.71-89.58 |

*FTIR analysis*

FTIR spectra of the DESs and their individual components are shown in Fig. S-1. The FTIR spectra of the tested DESs show a very strong and broad band at 3200-3500 cm-1 ascribed to *ν*(OH) stretching vibration, which confirms the existence of the hydrogen bonds in these mixtures. This band covers all bands belonging to the amine vibrations from TEOA and ChCl and has great intensity in every starting component of the DESs, except OLE, due to its long carbon chain that limits the formation of the intramolecular hydrogen bonds. The presence of *ν*(C-H) stretching bands at 2800-3000 cm-1 is obvious in the spectra of all DESs and their initial compounds,14 except OA. The band at 1550-1690 cm-1 in all spectra belongs to *δ*(OH) vibrations, overlapping the *δ*(NH3+) bands at 1660 and 1646 cm-1 in the spectra of TEOA and ChCl. The bands at 1403-1419 cm-1 and 1000-1117 cm-1 derived from *δ*(C-H) and *ν*(C-O) vibrations, respectively, are present in all spectra. The *ν*(C-N) bands at 1358,1350 and 1340 cm-1 present in the spectra of TEOA, ChCl and DMU are also present in all DESs that contain these components. In the spectra of AA, OA, LA and OLE, as well as of their DESs the *ν*(C=O) bands are at 1710-1730 cm-1.14 The FTIR analysis proved both the presence of the hydrogen bonds in these DESs and the characteristic functional groups of their constituents, showing no chemical changes (reactions) that occurred during their preparation.

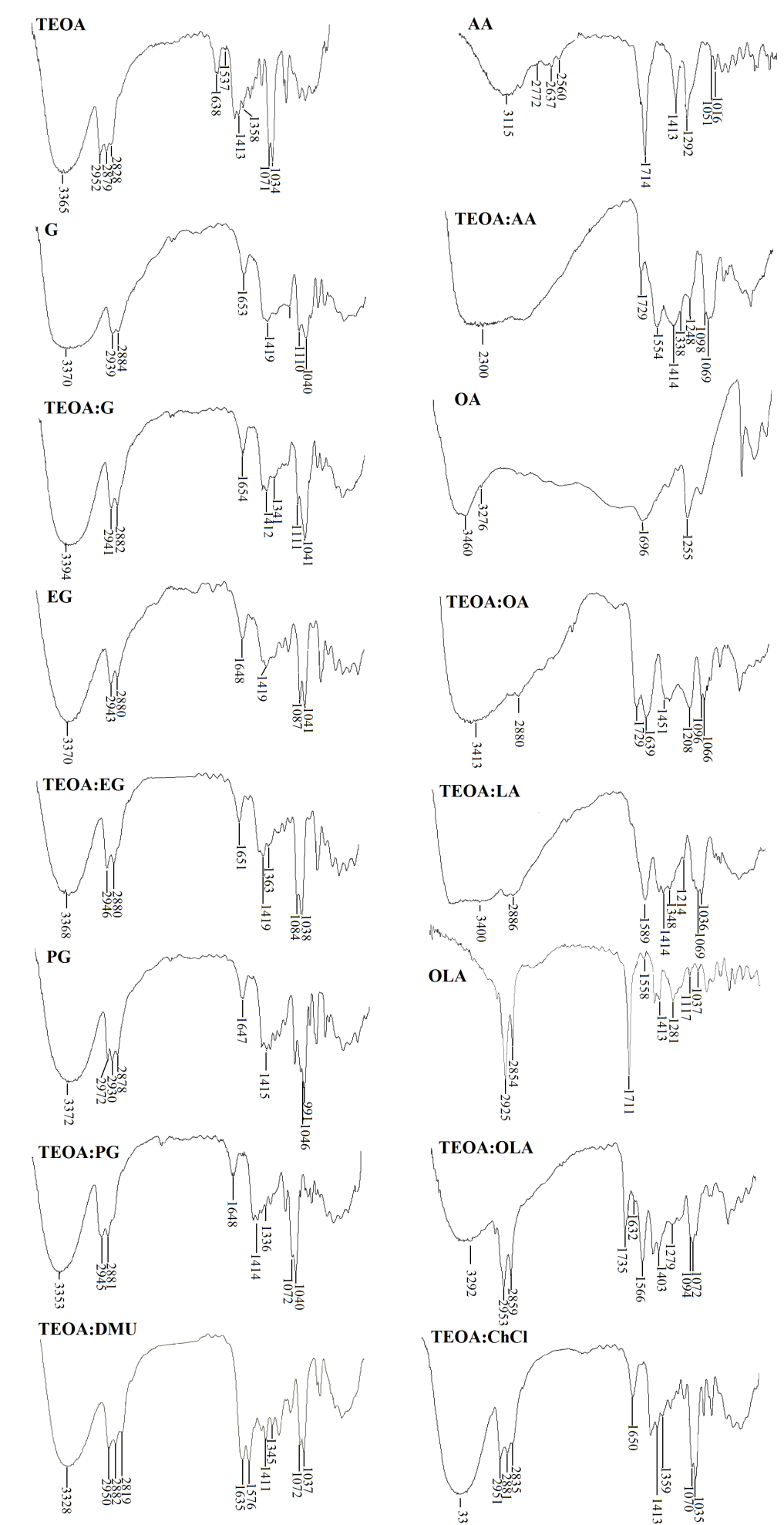


Fig. S-1. FTIR spectra of the DESs and their individual components at 25 °C in the region of 400-4000 cm-1.

*TGA and DSC analyses*

The TGA and DSC curves of the selected TEOA- and ChCl-based DESs with the same donors are shown in Fig. S-2. As can be seen in Fig. S-2, the TGA and DSC curves do not show any surprising behavior of the samples since no characteristic picks are present, except the certain mass loss evident from the TGA curves, within which one part refers certainly to water evaporation, explained by the higher upper limit of the temperature range.

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Fig. S-2. TGA and DSC curves recorded for: (a) TEOA:G, (b) TEOA:EG, (c) TEOA:PEG, (d) ChCl:TEOA, (e) ChCl:G, (f) ChCl:EG, (g) ChCl:PEG, at temperature range 298.15-343.15 K for (f) and (g) and 298.15-373.15 K for (a) – (e) and 101.325 kPa. Note: **–** denotes TGA curve, **–·–** denotes the first derivative of the TGA function, **––** denotes DSC curve and **–··–** denotes the first derivative of DSC function.

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1. \*Corresponding author. E-mail: ztodorovictfle@yahoo.com [↑](#footnote-ref-1)