

THE ROLE OF DES PRECURSORS AS HYDROTROPES: UNVEILING SYNERGISM/ANTAGONISM FOR ENHANCED KRAFT LIGNIN DISSOLUTION

Filipe H. B. Sosa¹, Dinis O. Abranches¹, André M. da Costa Lopes^{1,2}, Mariana C. da Costa³, João A. P. Coutinho^{1*}.

¹*CICECO, Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*

²*CECOLAB – Collaborative Laboratory Towards Circular Economy, R. Nossa Senhora da Conceição, Oliveira do Hospital, 3405-155, Portugal*

³*School of Chemical Engineering (FEQ), University of Campinas (UNICAMP), 13083-852, Campinas, São Paulo, Brazil.*

*Corresponding author. E-mail address: jcoutinho@ua.pt

Number of Pages: 6

Number of Tables: 3

Number of Figures: 2

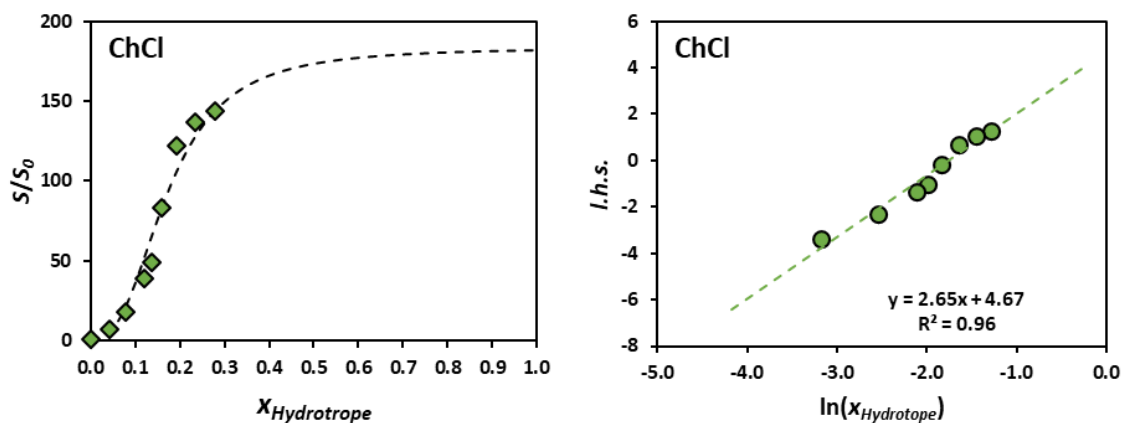


Figure S1. Left: solubility increase (S/S_0) of the Kraft Lignin in aqueous solutions of [ChCl] at 313.15 K (green diamond) along with the fitted curve of the cooperative hydrotrope model (- - -). Right: Experimental solubility data for Kraft lignin in aqueous solutions of [ChCl] at 313.15 K (green circles), in a linearized form (equation 1), where the y-axis represents the left-hand side (l.h.s) of equation 1 (- - -).

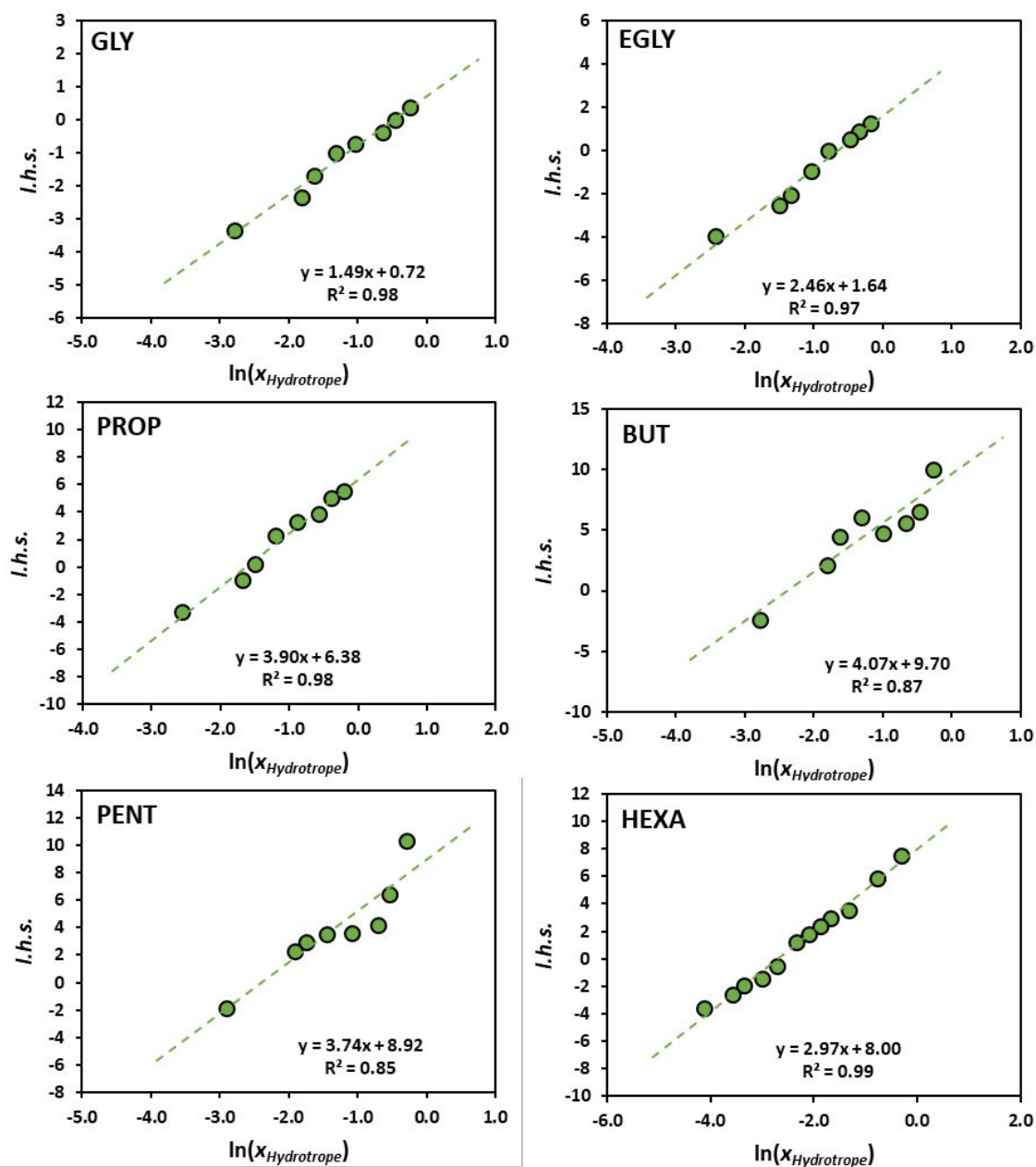


Figure S2. Experimental solubility data for Kraft lignin in aqueous solutions of GLY, EGLY, PROP, BUT, PENT, and HEXA at 313.15 K, in a linearized form (equation 1), where the y-axis represents the left-hand side (l.h.s.) of equation 1 (---).

Table S1. Setschenow Constants (K_S) for lignin in solvents

| System | K_S (kg/mol) |
|------------------|----------------------------------|
| Choline Chloride | 0.6444 |
| Glycerol | 0.1112 |
| Ethylene glycol | 0.1913 |
| 1,3-Propanediol | 0.2976 |
| 1,4-Butanediol | 0.4936 |
| 1,5-Pentanediol | 0.5752 |
| 1,6-Hexanediol | 1.6922 |
| ChCl:GLY | 0.2933 |
| ChCl:EGLY | 0.2978 |
| ChCl:PROP | 0.357 |
| ChCl:BUT | 0.6793 |
| ChCl:PENT | 0.9667 |
| ChCl:HEXA | 1.0344 |

Table S2. Parameters of the cooperative hydrotrophy model for the solubility of Kraft lignin in alcohols, [ChCl] and HBD hydrotrope solutions

| System | $(S/S_0)_{max}$ | m | b |
|------------------|-----------------------------------|----------|----------|
| Choline Chloride | 183 | 2.654 | 4.672 |
| Glycerol | 28 | 1.563 | 0.783 |
| Ethenediol | 288 | 2.459 | 1.640 |
| 1,3-Propanediol | 166 | 3.904 | 6.377 |
| 1,4-Butanediol | 176 | 4.068 | 9.696 |
| 1,5-Pentanediol | 184 | 3.739 | 8.917 |
| 1,6-Hexanediol | 204 | 2.970 | 7.997 |

Table S3. Solubility increase (S/S_0) of the Kraft Lignin in the studied aqueous solutions at 313.15 K.

| x_{water} | S/S_0 | x_{water} | S/S_0 | x_{water} | S/S_0 |
|--------------------------|-------------|--------------------------|-------------|--------------------------|-------------|
| [Ch]Cl:GLY (1:2) | | [Ch]Cl:PROP (1:2) | | [Ch]Cl:BUT (1:2) | |
| 0.212 | 167.17±3.73 | 0.218 | 137.60±3.16 | 0.232 | 148.30±3.02 |
| 0.459 | 146.08±0.87 | 0.484 | 136.55±0.97 | 0.475 | 148.57±5.02 |
| 0.618 | 130.91±1.70 | 0.640 | 136.13±0.22 | 0.659 | 147.44±3.52 |
| 0.722 | 90.48±1.10 | 0.741 | 132.24±1.71 | 0.756 | 144.60±1.40 |
| 0.800 | 36.28±0.83 | 0.814 | 58.61±2.25 | 0.823 | 137.02±0.51 |
| 0.829 | 25.50±0.91 | 0.844 | 29.64±3.30 | 0.850 | 123.50±1.83 |
| 0.936 | 4.95±1.23 | 0.942 | 7.30±0.31 | 0.898 | 33.22±1.87 |
| 1.000 | 1.00±0.35 | 1.000 | 1.00±0.35 | 0.932 | 13.75±0.39 |
| | | | | 0.947 | 9.95±0.21 |
| | | | | 1.000 | 1.00±0.35 |
| [Ch]Cl:PENT (1:2) | | [Ch]Cl:HEXA (1:2) | | [Ch]Cl:HEXA (1:1) | |
| 0.255 | 156.31±2.70 | 0.272 | 170.03±2.98 | 0.262 | 141.95±0.01 |
| 0.520 | 153.84±0.1 | 0.543 | 168.39±0.90 | 0.537 | 141.24±2.69 |
| 0.671 | 153.69±3.26 | 0.697 | 168.33±5.76 | 0.686 | 142.62±1.62 |
| 0.772 | 142.91±0.62 | 0.785 | 168.55±0.10 | 0.779 | 142.56±2.94 |
| 0.835 | 136.72±0.22 | 0.845 | 168.61±3.21 | 0.842 | 141.36±4.25 |
| 0.861 | 128.56±0.32 | 0.869 | 166.37±1.89 | 0.869 | 98.04±0.96 |
| 0.905 | 67.25±1.84 | 0.910 | 100.68±2.08 | 0.908 | 67.23±2.37 |
| 0.937 | 32.57±0.38 | 0.940 | 31.16±0.94 | 0.951 | 18.88±0.10 |
| 0.950 | 18.24±0.39 | 0.953 | 19.99±0.2 | 1.000 | 1.00±0.35 |
| 1.000 | 1.00±0.35 | 1.000 | 1.00±0.35 | | |
| [Ch]Cl:HEXA (1:3) | | HEXA | | [Ch]Cl | |
| 0.258 | 175.17±3.33 | 0.267 | 203.96±2.31 | 0.722 | 143.60±1.63 |
| 0.546 | 177.05±2.01 | 0.542 | 203.50±4.20 | 0.766 | 137.00±2.83 |
| 0.688 | 177.25±3.66 | 0.732 | 198.39±5.97 | 0.807 | 122.09±3.67 |
| 0.781 | 176.17±5.30 | 0.814 | 194.20±1.9 | 0.840 | 83.59±0.81 |
| 0.843 | 175.93±1.72 | 0.848 | 187.48±6.60 | 0.864 | 48.78±1.71 |
| 0.870 | 173.40±0.61 | 0.876 | 175.08±0.94 | 0.880 | 39.00±0.21 |
| 0.908 | 103.59±0.55 | 0.903 | 158.21±2.77 | 0.921 | 17.85±0.31 |
| 0.951 | 16.55±0.29 | 0.934 | 77.84±2.66 | 0.958 | 6.91±0.24 |
| 1.000 | 1.00±0.35 | 0.950 | 39.48±0.5 | 1.000 | 1.00±0.35 |
| | | 0.965 | 26.14±0.26 | | |
| | | 0.972 | 15.26±0.31 | | |
| | | 0.984 | 6.64±1.26 | | |
| | | 1.000 | 1.00±0.35 | | |

| x_{water} | S/S_0 | x_{water} | S/S_0 | x_{water} | S/S_0 |
|--------------------|-------------|--------------------|-------------|--------------------|-------------|
| GLY | | EGLY | | PROP | |
| 0.054 | 16.78±0.42 | 0.052 | 225.91±5.11 | 0.054 | 165.07±5.24 |
| 0.101 | 14.35±0.31 | 0.104 | 204.50±6.70 | 0.100 | 164.60±4.20 |
| 0.150 | 11.84±0.21 | 0.150 | 181.59±5.55 | 0.154 | 162.28±5.03 |
| 0.264 | 9.64±0.14 | 0.258 | 143.43±3.8 | 0.253 | 159.62±4.85 |
| 0.350 | 8.19±0.10 | 0.348 | 82.34±1.12 | 0.354 | 150.43±3.32 |
| 0.449 | 5.11±0.32 | 0.450 | 33.10±1.70 | 0.454 | 90.89±1.38 |
| 0.502 | 3.30±0.22 | 0.502 | 22.35±0.80 | 0.507 | 47.41±0.36 |
| 0.751 | 1.89±0.01 | 0.750 | 6.57±0.31 | 0.739 | 6.95±0.58 |
| 1.000 | 1.00±0.35 | 1.000 | 1.00±0.35 | 1.000 | 1.00±0.35 |
| BUT | | PENT | | | |
| 0.057 | 175.54±6.04 | 0.056 | 184.44±5.79 | | |
| 0.105 | 175.30±5.02 | 0.111 | 184.16±6.77 | | |
| 0.157 | 174.93±5.99 | 0.150 | 181.76±5.56 | | |
| 0.252 | 174.02±4.01 | 0.253 | 179.77±4.39 | | |
| 0.349 | 175.16±5.89 | 0.360 | 179.16±6.04 | | |
| 0.451 | 173.63±4.67 | 0.450 | 175.51±5.42 | | |
| 0.505 | 157.00±3.68 | 0.497 | 167.53±4.99 | | |
| 0.752 | 15.56±0.84 | 0.750 | 25.78±1.18 | | |
| 1.000 | 1.00±0.35 | 1.000 | 1.00±0.35 | | |