



Research article

# Thermodynamic investigations on host/guest complexation in deep eutectic solvent/water mixtures

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**Supplementary Table S1.** Thermodynamic parameters determined in the presence of 25 wt% of each DES component alone at 15, 25 and 35 °C

|                  | K (M <sup>-1</sup> ) |               |               | $\Delta H$ (kJ·mol <sup>-1</sup> ) |               |               | $-T\Delta S$ (kJ·mol <sup>-1</sup> ) |              |              | $\Delta G$ (kJ·mol <sup>-1</sup> ) |               |               |
|------------------|----------------------|---------------|---------------|------------------------------------|---------------|---------------|--------------------------------------|--------------|--------------|------------------------------------|---------------|---------------|
|                  | 15 °C                | 25 °C         | 35 °C         | 15 °C                              | 25 °C         | 35 °C         | 15 °C                                | 25 °C        | 35 °C        | 15 °C                              | 25 °C         | 35 °C         |
| ChCl             | 30,000 ± 2000        | 23,000 ± 2000 | 18,000 ± 1000 | -17.13 ± 0.94                      | -19.93 ± 1.13 | -22.90 ± 1.36 | -7.58 ± 1.13                         | -4.98 ± 1.32 | -2.13 ± 1.56 | -24.71 ± 0.20                      | -24.91 ± 0.20 | -25.03 ± 0.20 |
| Urea             | 41,000 ± 2000        | 29,000 ± 1000 | 20,000 ± 900  | -25.02 ± 0.72                      | -26.96 ± 0.81 | -29.03 ± 0.93 | -0.45 ± 0.83                         | 1.51 ± 0.93  | 3.66 ± 1.05  | -25.47 ± 0.20                      | -25.45 ± 0.20 | -25.37 ± 0.20 |
| Glycerol         | 23,000 ± 1000        | 17,000 ± 1000 | 11,600 ± 600  | -23.23 ± 0.75                      | -26.13 ± 0.89 | -29.19 ± 1.07 | -0.89 ± 0.88                         | 2.03 ± 1.02  | 5.21 ± 1.21  | -24.12 ± 0.20                      | -24.10 ± 0.20 | -23.98 ± 0.20 |
| Xylitol          | 33,000 ± 2000        | 24,000 ± 1000 | 16,700 ± 900  | -23.01 ± 0.75                      | -25.77 ± 0.14 | -28.56 ± 0.17 | -1.94 ± 0.87                         | 0.80 ± 0.27  | 3.66 ± 0.30  | -24.95 ± 0.20                      | -24.97 ± 0.20 | -24.90 ± 0.20 |
| Sorbitol         | 47,000 ± 2000        | 34,000 ± 2000 | 24,000 ± 1000 | -23.40 ± 0.71                      | -26.15 ± 0.82 | -29.00 ± 0.96 | -2.40 ± 0.82                         | 0.32 ± 0.94  | 3.22 ± 0.94  | -25.80 ± 0.20                      | -25.83 ± 0.20 | -25.77 ± 0.20 |
| Butane-1,3-diol  | 2900 ± 400           | 2000 ± 300    | 1400 ± 200    | -24.92 ± 1.46                      | -27.11 ± 1.77 | -29.41 ± 2.26 | 5.80 ± 1.83                          | 8.22 ± 2.16  | 10.83 ± 2.66 | -19.12 ± 0.40                      | -18.89 ± 0.40 | -18.58 ± 0.40 |
| Propane-1,3-diol | 5200 ± 600           | 3800 ± 400    | 2700 ± 300    | -21.70 ± 1.19                      | -24.33 ± 1.45 | -27.04 ± 1.82 | 1.16 ± 1.45                          | 3.87 ± 1.71  | 6.76 ± 2.09  | -20.53 ± 0.30                      | -20.45 ± 0.30 | -20.28 ± 0.30 |
| Glucose          | 64,000 ± 3000        | 44,000 ± 2000 | 30,000 ± 1000 | -25.40 ± 0.63                      | -28.38 ± 0.72 | -31.40 ± 0.84 | -1.13 ± 0.72                         | 1.86 ± 0.82  | 4.99 ± 0.94  | -26.53 ± 0.10                      | -26.52 ± 0.10 | -26.41 ± 0.10 |
| Fructose         | 35,000 ± 2000        | 27,000 ± 2000 | 20,000 ± 1000 | -18.94 ± 0.81                      | -22.47 ± 0.20 | -26.04 ± 0.23 | -6.17 ± 0.97                         | -2.79 ± 0.35 | 0.74 ± 0.39  | -25.11 ± 0.20                      | -25.26 ± 0.20 | -25.29 ± 0.20 |



**Supplementary Table S3.** Thermodynamic parameters determined in water, in the different DES/water mixtures as well as in ethanol/water mixtures at 25 °C

| Water<br>Solvent      | $K_f$ ( $M^{-1}$ ) |               |              |               |               | $\Delta H$ ( $kJ \cdot mol^{-1}$ ) |              |              |              |               | $-T\Delta S$ ( $kJ \cdot mol^{-1}$ ) |               |               |               |               | $\Delta G$ ( $kJ \cdot mol^{-1}$ ) |               |               |  |  |
|-----------------------|--------------------|---------------|--------------|---------------|---------------|------------------------------------|--------------|--------------|--------------|---------------|--------------------------------------|---------------|---------------|---------------|---------------|------------------------------------|---------------|---------------|--|--|
|                       | 25 wt%             | 50 wt%        | 70 wt%       | 25 wt%        | 50 wt%        | 70 wt%                             | 25 wt%       | 50 wt%       | 70 wt%       | 25 wt%        | 50 wt%                               | 70 wt%        | 25 wt%        | 50 wt%        | 70 wt%        | 25 wt%                             | 50 wt%        | 70 wt%        |  |  |
| ChCl:Urea             | 30,000 ± 2000      | 21,000 ± 1000 | 12,100 ± 700 | -24.86 ± 0.87 | -27.05 ± 0.84 | -27.28 ± 0.99                      | -0.66 ± 1.00 | 2.41 ± 0.96  | 3.98 ± 1.13  | -25.51 ± 0.20 | -24.64 ± 0.20                        | -23.29 ± 0.20 | -25.51 ± 0.20 | -24.64 ± 0.20 | -23.29 ± 0.20 | -25.51 ± 0.20                      | -24.64 ± 0.20 | -23.29 ± 0.20 |  |  |
| ChCl:Glycerol         | 21,000 ± 1000      | 10,500 ± 600  | 5600 ± 300   | -23.99 ± 0.95 | -26.67 ± 0.95 | -30.11 ± 1.01                      | -0.64 ± 1.10 | 3.72 ± 1.10  | 8.70 ± 1.16  | -24.63 ± 0.20 | -22.95 ± 0.20                        | -21.41 ± 0.20 | -24.63 ± 0.20 | -22.95 ± 0.20 | -21.41 ± 0.20 | -24.63 ± 0.20                      | -22.95 ± 0.20 | -21.41 ± 0.20 |  |  |
| ChCl:Xylitol          | 28,000 ± 2000      | 17,000 ± 1000 | ND           | -24.14 ± 0.91 | -24.93 ± 0.95 | ND                                 | -1.24 ± 1.05 | 0.78 ± 1.09  | ND           | -25.38 ± 0.20 | -24.15 ± 0.20                        | ND            | -25.38 ± 0.20 | -24.15 ± 0.20 | ND            | -25.38 ± 0.20                      | -24.15 ± 0.20 | ND            |  |  |
| ChCl:Sorbitol         | 31,000 ± 2000      | 19,000 ± 1000 | ND           | -24.76 ± 0.88 | -24.39 ± 0.94 | ND                                 | -0.83 ± 1.01 | 0.01 ± 1.09  | ND           | -25.59 ± 0.20 | -24.38 ± 0.20                        | ND            | -25.59 ± 0.20 | -24.38 ± 0.20 | ND            | -25.59 ± 0.20                      | -24.38 ± 0.20 | ND            |  |  |
| ChCl:Butane-1,3-diol  | 4300 ± 500         | 1500 ± 300    | 500 ± 20     | -21.68 ± 1.59 | -25.30 ± 2.41 | -27.28 ± 0.57                      | 0.93 ± 1.88  | 7.23 ± 2.99  | 11.72 ± 0.65 | -20.75 ± 0.30 | -18.06 ± 0.60                        | -15.56 ± 0.10 | -20.75 ± 0.30 | -18.06 ± 0.60 | -15.56 ± 0.10 | -20.75 ± 0.30                      | -18.06 ± 0.60 | -15.56 ± 0.10 |  |  |
| ChCl:Propane-1,3-diol | 10,100 ± 800       | 4300 ± 400    | 2600 ± 400   | -21.75 ± 1.17 | -23.84 ± 1.39 | -24.32 ± 1.68                      | -1.10 ± 1.37 | 3.08 ± 1.64  | 4.82 ± 2.02  | -22.85 ± 0.30 | -20.76 ± 0.30                        | -19.50 ± 0.40 | -22.85 ± 0.30 | -20.76 ± 0.30 | -19.50 ± 0.40 | -22.85 ± 0.30                      | -20.76 ± 0.30 | -19.50 ± 0.40 |  |  |
| ChCl:Glucose          | 31,000 ± 2000      | 15,000 ± 1000 | ND           | -22.45 ± 0.97 | -21.21 ± 1.14 | ND                                 | -3.17 ± 1.12 | -2.66 ± 1.33 | ND           | -25.62 ± 0.20 | -23.86 ± 0.20                        | ND            | -25.62 ± 0.20 | -23.86 ± 0.20 | ND            | -25.62 ± 0.20                      | -23.86 ± 0.20 | ND            |  |  |
| ChCl:Fructose         | 26,000 ± 2000      | 12,500 ± 100  | ND           | -21.89 ± 0.24 | -20.79 ± 0.04 | ND                                 | -3.34 ± 0.41 | -2.64 ± 0.06 | ND           | -25.23 ± 0.20 | -23.43 ± 0.10                        | ND            | -25.23 ± 0.20 | -23.43 ± 0.10 | ND            | -25.23 ± 0.20                      | -23.43 ± 0.10 | ND            |  |  |
| Ethanol               | 1700 ± 100         | 1800 ± 400    | 100 ± 10     | -55.66 ± 1.12 | -43.47 ± 2.01 | -12.85 ± 5.56                      | 37.24 ± 1.32 | 24.95 ± 2.53 | 0.75 ± 5.71  | -18.42 ± 0.20 | -18.52 ± 0.60                        | -12.10 ± 0.20 | -18.42 ± 0.20 | -18.52 ± 0.60 | -12.10 ± 0.20 | -18.42 ± 0.20                      | -18.52 ± 0.60 | -12.10 ± 0.20 |  |  |

