

**Supporting information**

**Distribution coefficients of furfural and  
5-hydroxymethylfurfural in hydrophobic deep eutectic solvent  
+ water systems: Experiments and PC-SAFT predictions**

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Table S1. Pure-component PC-SAFT parameters for DESs, water, FF and HMF. FF was considered as non self-associating non-polar compound; cross-association was allowed between FF and all other components (“induced-association” approach). All other components were modeled as associating non-polar compound using the 2B association scheme.

| Compounds    | $M_w/\text{g}\cdot\text{mol}^{-1}$ | $m_{\text{seg},i}$ | $\sigma_i/\text{\AA}$ | $u_i/k_B$ (K) | $N_{\text{site}}$ | $\varepsilon^{\text{AiBi}}/k_B$ (K) | $k^{\text{AiBi}}$ |
|--------------|------------------------------------|--------------------|-----------------------|---------------|-------------------|-------------------------------------|-------------------|
| deca-lid 4:1 | 247.17                             | 5.588              | 4.072                 | 273.16        | 1 + 1             | 3952                                | 0.00006           |
| deca-lid 3:1 | 201.54                             | 6.479              | 3.591                 | 247.80        | 1 + 1             | 2818                                | 0.007             |
| deca-lid 2:1 | 192.95                             | 6.802              | 3.473                 | 249.44        | 1 + 1             | 2423                                | 0.013             |
| deca-men     | 164.27                             | 4.897              | 3.721                 | 229.72        | 1 + 1             | 2682                                | 0.096             |
| deca-thy     | 161.24                             | 3.756              | 4.071                 | 332.09        | 1 + 1             | 3909                                | 0.00004           |
| deca-n8888Br | 297.10                             | 15.482             | 3.158                 | 317.42        | 1 + 1             | 5000                                | 0.010             |
| thy-lid      | 178.26                             | 6.214              | 3.419                 | 222.82        | 1 + 1             | 2409                                | 0.096             |
| water        | 18.02                              | 1.205              | 2.793                 | 353.95        | 1 + 1             | 2426                                | 0.045             |
| FF           | 96.08                              | 3.071              | 3.356                 | 320.08        | 1 + 1             | 0                                   | 0.045             |
| HMF          | 126.44                             | 2.310              | 4.038                 | 320.38        | 1 + 1             | 3168                                | 0.001             |

Table S2. Extraction coefficient of pure wt% HMF + 1wt% FF in different shaking times 5-10-20-30-60min at temperature 298K, solvent to feed ratio 1:1.

| Time (min) | K   |     |
|------------|-----|-----|
|            | FF  | HMF |
| 5          | 4,6 | 1,6 |
| 10         | 4,6 | 1,8 |
| 20         | 4,7 | 1,6 |
| 30         | 4,6 | 1,7 |
| 60         | 4,7 | 1,6 |

\*Standard uncertainties are  $u(T) = 1$  K,  $u(p) = 0.03$  bar,  $u(K) = 0.2$

Table S3. Distribution coefficients obtained by extraction with ten different DESs at different 298 K) at 1.01 bar from a starting solution consisting of 1wt% FF /HMF at solvent-to-feed ratio 1:1.

| DES          | K-value FF | K-Value HMF |
|--------------|------------|-------------|
| deca-N8888br | 4.1        | 1.5         |
| deca-men     | 2.5        | 0.3         |
| deca-thy     | 12.0       | 1.7         |
| deca-atr     | 0.8        | 0.8         |
| dode-atr     | 0.8        | 0.9         |
| deca-lid 2:1 | 3.3        | 1.4         |
| deca-lid 3:1 | 3.2        | 1.0         |
| deca-lid 4:1 | 3.1        | 0.8         |
| thy-lid      | 9.6        | 1.4         |
| dode-lid     | 1.5        | 1.1         |

\*Standard uncertainties are  $u(T) = 1$  K,  $u(p) = 0.03$  bar,  $u(K) = 0.2$

Table S4. Kamlet taft paramters for the 10 different DESs and toluene and ethanol as reference from literature.

|                  | Et(30) | EtN   | $\pi$ | $\alpha$ | $\beta$ |
|------------------|--------|-------|-------|----------|---------|
| ethanol          | 51.984 | 0.657 | 0.528 | 0.936    | 0.681   |
| Toluene          | 71.122 | 1.248 | 0.652 | 1.573    | 0.564   |
| Deca-lid 2-1     | 54.459 | 0.733 | 0.87  | 1.018    | 1.661   |
| Deca-lid 3-1     | 54.459 | 0.733 | 1.021 | 1.018    | 0.761   |
| Deca-lid 4-1     | 54.459 | 0.733 | 1.184 | 1.018    | 0.214   |
| Deca-Thy 1-1     | 52.364 | 0.669 | 0.422 | 0.948    | 0.587   |
| Deca-N8888Br 2-1 | 60.192 | 0.91  | 1.99  | 1.209    | 0.232   |
| Deca-ATR 2-1     | 60.446 | 0.918 | 0.652 | 1.218    | 0.107   |
| Deca-Men 1-1     | 51.515 | 0.642 | 0.831 | 0.92     | 0.176   |
| Dode-lid 2-1     | 54.877 | 0.746 | 0.632 | 1.032    | 0.465   |
| Dode-ATR 2-1     | 60.703 | 0.926 | 0.632 | 1.226    | 0.084   |
| Thy-Lid 2-1      | 62.02  | 0.967 | 0.752 | 1.27     | 0.385   |

Table S5. Distribution coefficients obtained by extraction with four selected DESs at 298K) at 1.01 bar from different starting solution consisting of 0.1-0.2-0.3-0.4-0.5-0.6-0.7-0.8-0.9-1.0wt% FF/HMF at solvent-to-feed ratio 1:1.

| conc<br>wt% | K FF         |              |                  |         | K HMF        |              |                  |         |
|-------------|--------------|--------------|------------------|---------|--------------|--------------|------------------|---------|
|             | deca-<br>thy | deca-<br>men | deca-<br>N8888Br | thy-lid | deca-<br>thy | deca-<br>men | deca-<br>N8888Br | thy-lid |
| 0.1         | 11.4         | 2.2          | 3.6              | 9.7     | 1.7          | 0.3          | 1.5              | 1.3     |
| 0.2         | 10.9         | 2.1          | 2.0              | 9.7     | 1.7          | 0.3          | 1.5              | 1.4     |
| 0.3         | 11.4         | 2.2          | 2.1              | 9.6     | 1.7          | 0.3          | 1.5              | 1.3     |
| 0.4         | 11.4         | 2.1          | 2.0              | 9.6     | 1.7          | 0.3          | 1.5              | 1.3     |
| 0.5         | 11.5         | 2.2          | 2.2              | 9.7     | 1.8          | 0.3          | 1.5              | 1.4     |
| 0.6         | 11.8         | 2.2          | 3.9              | 9.5     | 1.7          | 0.3          | 1.5              | 1.4     |
| 0.7         | 11.5         | 2.1          | 3.7              | 9.6     | 1.7          | 0.3          | 1.5              | 1.3     |
| 0.8         | 11.2         | 2.2          | 3.6              | 9.8     | 1.7          | 0.3          | 1.5              | 1.3     |
| 0.9         | 11.2         | 2.2          | 3.6              | 9.6     | 1.7          | 0.4          | 1.5              | 1.3     |
| 1           | 11.1         | 2.1          | 3.6              | 9.6     | 1.7          | 0.3          | 1.5              | 1.4     |

\*Standard uncertainties are  $u(T) = 1$  K.  $u(p) = 0.03$  bar.  $u(K) = 0.2$

Table S6. Distribution coefficients obtained by extraction with four selected DESs at 298K) at 1.01 bar from different starting solution consisting of 1.0-3.0-5.0 wt% FF and 1.0-10.0-20.0wt% HMF at solvent-to-feed ratio 1:1.

| DES          | 1 wt% FF | 3 wt% FF | 5 wt% FF | 1 wt% HMF | 10 wt% HMF | 20 wt% HMF |
|--------------|----------|----------|----------|-----------|------------|------------|
| deca-men     | 2.1      | 2.2      | 4.1      | 0.3       | 0.3        | 0.39       |
| deca-thy     | 11.1     | 10.3     | 11.4     | 1.7       | 1.8        | 1.7        |
| thy-lid      | 9.6      | 8.4      | 9.9      | 1.4       | 1.4        | 1.1        |
| deca-n8888Br | 3.6      | 4.3      | 5.9      | 1.5       | 0.8        | 1.1        |

\*Standard uncertainties are  $u(T) = 1$  K.  $u(p) = 0.03$  bar.  $u(K) = 0.2$

Table S7. Distribution coefficient from FF in a ternary LLE system (DES/H<sub>2</sub>O/FF)

| DES          | $K_{exp}$ | $k_{DES:water=0}$ |
|--------------|-----------|-------------------|
| deca-lid 2:1 | 3.28      | 1.97              |
| deca-lid 3:1 | 3.17      | 2.6               |
| deca-lid 4:1 | 3.09      | 2.17              |
| deca-men     | 2.12      | 2.73              |
| deca-thy     | 11.06     | 7.28              |
| thy-lid      | 9.63      | 3.75              |
| deca-N8888Br | 3.63      | 3.55              |

\*Calculations with  $k(DES.H_2O)$  fitted to LLE.  $K(FF.H_2O)=-0.007$  and  $k(DES.FF)=0$

Table S8. Distribution coefficient from HMF in a ternary LLE system (DES/H<sub>2</sub>O/HMF)

| DES          | $K_{\text{exp}}$ | $k_{\text{DES:water}=0}$ | $k_{\text{DES:water} \neq 0}$ | $k_{\text{DES:HMF} \neq 0}$ |
|--------------|------------------|--------------------------|-------------------------------|-----------------------------|
| deca-lid 2:1 | 1.40             | 0.88                     | 0.66                          | -                           |
| deca-lid 3:1 | 1.00             | 0.76                     | 0.71                          | -                           |
| deca-lid 4:1 | 0.82             | 0.42                     | 0.41                          | -                           |
| deca-men     | 0.32             | 0.80                     | 0.78                          | -                           |
| deca-thy     | 1.73             | 0.70                     | 0.67                          | 1.74                        |
| thy-lid      | 1.35             | 1.13                     | 0.25                          | 1.35                        |
| deca-N8888Br | 1.48             | 0.15                     | 0.66                          | 1.48                        |

Table S9.  $k_{ij}$  values between water+HMF. water+FF. water+DES and between HMF+DES used in this work.

| Pair               | $k_{ij}$ | Reference                                  |
|--------------------|----------|--------------------------------------------|
| HMF /water         | -0.042   | 32                                         |
| FF/water           | -0.01    | This work. fitted to LLE FF-water (see SI) |
| deca-lid 4:1/water | -0.0633  | 24                                         |
| deca-lid 3:1/water | -0.0518  | 24                                         |
| deca-lid 2:1/water | -0.0645  | 24                                         |
| deca-men /water    | 0.0417   | 24                                         |
| deca-thy /water    | 0.028    | 24                                         |
| deca-n8888Br/water | 0.0184   | 24                                         |
| thy-lid /water     | 0.0655   | 24                                         |
| deca-thy /HMF      | -0.0318  | 24                                         |
| deca-n8888Br / HMF | -0.0485  | 24                                         |
| thy-lid /HMF       | 0.0065   | 24                                         |