An overview of the biphasic dehydration of sugars to 5-hydroxymethylfurfural and furfural: a rational selection of solvents using COSMO-RS and selection guides.

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S1. Experimental procedure for the measurement of the distribution of 5-hydroxymethylfurfural and furfural

Materials

The following chemicals were used for the partition experiments: 5-hydroxymethylfurfural (Fluorochem, 98%), furfural (Sigma Aldrich, 99%), methyl propionate (Abcr GmbH, 99%), ethyl acetate (Carl Roth, ≥99.5%). In addition, milliQ water was used as filtered by Merck Millipak 0.22 μm (resistivity of 18.2 MΩ.cm).

Partition experiments

The partition of 5-HMF and furfural in aqueous biphasic media was performed putting in contact an aqueous phase containing the furan with ethyl acetate or methyl propionate as organic extracting phases. The experiments were performed in 10 mL magnetically stirred vials for microwave reactions, with reinforced glass walls to withstand higher pressures than conventional glassware.

Four different chemical compositions of the loads were tested for partition. As aqueous phases, 1.25 mL of MilliQ water solutions containing 0.7% wt. and 7% wt. of 5-HMF (corresponding to the theoretical maximum 5-HMF that could be obtained from 1% wt. and 10 % wt. of fructose) were prepared. In the case of furfural, 0.64% wt. and 6.4% wt. were added to 1.5 mL of MilliQ water (likewise, corresponding to the theoretical maximum furfural obtained from 1% wt. and 10% wt. solutions of xylose). As organic phases, 4.09 mL of methyl propionate and 4.16 mL of ethyl acetate were used (3.75 g of each), which were put in contact with the two different aqueous solutions of 5-HMF and the two of furfural.

The distribution of 5-HMF and furfural from the described four batches was performed at the temperatures of 25 °C and 150 °C. For the experiments at 25 °C, the tubes containing the biphasic systems were placed into an oil bath on a heating plate (IKA RCT basic, accuracy ±0.05 °C) magnetically stirred at 1200 rpm during 4 hours. After stirring stopped, the batches were allowed to settle at least 12 h. In the case of the experiments at 150 °C, owing to the operation exceeding the boiling points of both water and the organic solvents, the experiments were conducted in an Anton Paar Monowave 450 microwave reactor. The pressures reached during these experiments ranged between 9 and 10 bar. On this occasion, owing to the potential sensitivity to thermal degradation of the furans, the partition experiment was performed only for 15 min. at 150 °C under stirred conditions, then was allowed to settle another 15 min. at this temperature without stirring and subsequently allowed to settle further 12 h at room conditions out of the microwave reactor.

Finally, samples were withdrawn from the organic-rich (top) and aqueous (bottom) phases with needles and taken for analysis.

Analytical methods

The organic-rich phase was analyzed using a Shimadzu GC-2030 GC device equipped with a flame ionization detector (FID). Resolution of the peaks was achieved with a Restek Rtx-1701 column (30 m x 0.25 mm x 0.25 μm) using He as carrier gas with an injector temperature of 260 °C and FID temperature at 260 °C. The temperature program followed started holding during 6 minutes at 140 °C, followed by a ramp of 25 °C/min up to 250 °C and finally this temperature was held during 5 minutes.

For its part, the aqueous phase was analyzed using HPLC employing a Shimadzu LC-20AD device equipped with a diode array detector (SPD-M20A). Separation was made using an Organic-Acid Resin
column (300 m x 8 mm) supplied by Chromatographie-Service GmbH employing acidic water as mobile phase (2 mM trifluoroacetic acid solution in MilliQ water) pumping at 1 mL/min through the column, which was kept at 40°C for separation in a CTO-10AS oven. Detection of 5-HMF was made at 277 nm and furfural at 282 nm.

References

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Figure S1. Experimental and COSMO-RS predictions of the liquid-liquid equilibria of different \((H_2O + 5\text{-HMF} + \text{solvent})\) systems at different temperatures.
Figure S2. Experimental and COSMO-RS predictions of the liquid-liquid equilibria of different \{H_2O + furfural + solvent\} systems at different temperatures.
Figure S3. Probability of solubility of 5-HMF in the entire set of solvents showing miscibility gap with water at 150 °C as predicted from the relative solvent screening by COSMO-RS
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Table S1. List of candidates for the biphasic dehydration of sugars to furans from different solvent guides in literature and COSMO-RS predictions of miscibility with water at 298.15, 373.15 and 423.15 K

| Solvent             | CAS    | Miscibility gap predicted? | $w_{\text{H}_2\text{O}}$ | $w_{\text{solvent}}$ | $w_{\text{H}_2\text{O}}$ | $w_{\text{solvent}}$ | $w_{\text{H}_2\text{O}}$ | $w_{\text{solvent}}$ |
|---------------------|--------|-----------------------------|---------------------------|----------------------|---------------------------|----------------------|---------------------------|----------------------|
| Alcohols            |        |                             | T= 298.15 K               | T= 423.15 K          |                           |                      |                           |                      |
| methanol            | 67-56-1| No                          |                           |                      |                           |                      |                           |                      |
| ethanol             | 64-17-5| No                          |                           |                      |                           |                      |                           |                      |
| propanol            | 71-23-8| No                          |                           |                      |                           |                      |                           |                      |
| 2-propanol          | 67-63-0| No                          |                           |                      |                           |                      |                           |                      |
| ethylene glycol     | 107-21-1| No                        |                           |                      |                           |                      |                           |                      |
| propylene glycol    | 57-55-6| No                          |                           |                      |                           |                      |                           |                      |
| 1,3-propanediol     | 504-63-2| No                        |                           |                      |                           |                      |                           |                      |
| glycerol            | 56-81-5| No                          |                           |                      |                           |                      |                           |                      |
| 1-butanol           | 71-36-3| Yes                         | 0.2315                    | 0.7685               | 0.9608                    | 0.0392               | 0.2802                    | 0.7198               | 0.9401               | 0.0599               |
| 2-butanol           | 78-92-2| Yes                         | 0.2262                    | 0.7738               | 0.9593                    | 0.0407               | 0.2591                    | 0.7409               | 0.9428               | 0.0572               |
| isobutanol          | 78-83-1| Yes                         | 0.1998                    | 0.8002               | 0.9622                    | 0.0378               | 0.2650                    | 0.7350               | 0.9383               | 0.0617               |
| tert-butanol        | 75-65-0| Yes                         | 0.2580                    | 0.7420               | 0.9476                    | 0.0524               | 0.2893                    | 0.7107               | 0.9278               | 0.0722               |
| glycerol formal     | 5464-28-8| No                       |                           |                      |                           |                      |                           |                      |                      |
| 3-methoxy-1,2-propanediol | 623-39-2| No                        |                           |                      |                           |                      |                           |                      |                      |
| 1-pentanol          | 71-41-0| Yes                         | 0.1404                    | 0.8596               | 0.9869                    | 0.0131               | 0.1800                    | 0.8200               | 0.9768               | 0.0232               |
| isopentanol         | 123-51-3| Yes                        | 0.1416                    | 0.8584               | 0.9836                    | 0.0164               | 0.1897                    | 0.8103               | 0.9703               | 0.0297               |
| 2-methyl-2-butanol  | 75-85-4| Yes                         | 0.1274                    | 0.8726               | 0.9843                    | 0.0157               | 0.1612                    | 0.8388               | 0.9735               | 0.0265               |
| tetrahydrofurfuryl alcohol | 97-99-4| Not at all temperatures      |                           |                      |                           |                      |                           |                      |                      |
| furfuryl alcohol    | 98-00-0| Yes                         | 0.1824                    | 0.8176               | 0.9226                    | 0.0774               | 0.4144                    | 0.5856               | 0.7708               | 0.2292               |
| 1,3-dimethoxy-2-propanol | 623-69-8| No                        |                           |                      |                           |                      |                           |                      |                      |
| 1-hexanol           | 111-27-3| Yes                        | 0.0953                    | 0.9047               | 0.9955                    | 0.0045               | 0.1300                    | 0.8700               | 0.9901               | 0.0099               |
| 3-methoxy-3-methylbutanol | 56539-66-3| Yes                     | 0.4129                    | 0.5871               | 0.9119                    | 0.0881               | 0.2215                    | 0.7785               | 0.9559               | 0.0441               |
| solketal            | 100-79-8| No                          |                           |                      |                           |                      |                           |                      |                      |
| 1-heptanol          | 111-70-6| Yes                        | 0.0688                    | 0.9312               | 0.9985                    | 0.0015               | 0.0985                    | 0.9015               | 0.9958               | 0.0042               |
| benzyl alcohol      | 100-51-6| Yes                        | 0.1022                    | 0.8978               | 0.9741                    | 0.0259               | 0.2021                    | 0.7979               | 0.9353               | 0.0647               |
1-octanol | 111-87-5 | Yes | 0.0520 | 0.9480 | 0.9995 | 0.0005 | 0.0783 | 0.9217 | 0.9982 | 0.0018 |
1-decanol | 112-30-1 | Yes | 0.0336 | 0.9664 | 0.9999 | 0.0001 | 0.0552 | 0.9448 | 0.9997 | 0.0003 |
dihydroneocanol | 53219-21-9 | Yes | 0.0330 | 0.9670 | 0.9998 | 0.0002 | 0.0550 | 0.9450 | 0.9990 | 0.0010 |
geraniol | 106-24-1 | Yes | 0.0469 | 0.9531 | 0.9994 | 0.0006 | 0.0744 | 0.9256 | 0.9978 | 0.0022 |
dihydro terpineol | 58985-02-7 | Yes | 0.0422 | 0.9578 | 0.9993 | 0.0007 | 0.0598 | 0.9402 | 0.9977 | 0.0023 |
-terpineol | 98-55-5 | Yes | 0.0341 | 0.9659 | 0.9992 | 0.0008 | 0.0593 | 0.9407 | 0.9971 | 0.0029 |
β-terpineol | 138-87-4 | Yes | 0.0319 | 0.9681 | 0.9992 | 0.0008 | 0.0607 | 0.9393 | 0.9969 | 0.0031 |
nopol | 128-50-7 | Yes | 0.0414 | 0.9586 | 0.9992 | 0.0008 | 0.0588 | 0.9412 | 0.9973 | 0.0027 |
oleyl alcohol | 143-28-2 | Yes | 0.0109 | 0.9891 | 1.0000 | 0.0000 | 0.0248 | 0.9752 | 1.0000 | 0.0000 |

**Esters**

methyl formate | 107-31-3 | No | | | | | | | | |
methyl acetate | 79-20-9 | Yes | 0.2399 | 0.7701 | 0.9115 | 0.0885 | 0.4388 | 0.5612 | 0.7476 | 0.2524 |
ethyl acetate | 141-78-6 | Yes | 0.1423 | 0.8577 | 0.9095 | 0.0905 | 0.1977 | 0.8023 | 0.9369 | 0.0631 |
isopropyl acetate | 108-21-4 | Yes | 0.0631 | 0.9369 | 0.9778 | 0.0222 | 0.1206 | 0.8794 | 0.9769 | 0.0231 |
n-propyl acetate | 109-60-4 | Yes | 0.0604 | 0.9396 | 0.9800 | 0.0200 | 0.1190 | 0.8810 | 0.9792 | 0.0208 |
n-butyl acetate | 123-86-4 | Yes | 0.0367 | 0.9633 | 0.9937 | 0.0063 | 0.0860 | 0.9140 | 0.9913 | 0.0087 |
n-pentyl acetate | 628-63-7 | Yes | 0.0242 | 0.9758 | 0.9981 | 0.0019 | 0.0657 | 0.9343 | 0.9965 | 0.0035 |
isoamyl acetate | 123-92-2 | Yes | 0.0284 | 0.9716 | 0.9969 | 0.0031 | 0.0711 | 0.9289 | 0.9951 | 0.0049 |
geranyl acetate | 105-67-3 | Yes | 0.0057 | 0.9943 | 1.0000 | 0.0000 | 0.0302 | 0.9698 | 0.9999 | 0.0001 |
adipic acid diethyl ester | 141-28-6 | Yes | 0.0242 | 0.9758 | 0.9975 | 0.0025 | 0.0685 | 0.9315 | 0.9973 | 0.0027 |
ethyl palmitate | 628-97-7 | Yes | 0.0023 | 0.9977 | 1.0000 | 0.0000 | 0.0150 | 0.9850 | 1.0000 | 0.0000 |
acetic anhydride | 108-24-7 | Yes | 0.0363 | 0.9637 | 0.9392 | 0.0608 | 0.2502 | 0.7498 | 0.8541 | 0.1459 |
methyl propionate | 554-12-1 | Yes | 0.0812 | 0.9188 | 0.9431 | 0.0569 | 0.1716 | 0.8284 | 0.9454 | 0.0546 |
isobutyl acetate | 110-19-0 | Yes | 0.0394 | 0.9606 | 0.9921 | 0.0079 | 0.0884 | 0.9116 | 0.9897 | 0.0103 |
dibutyl sebacate | 109-43-3 | Yes | 0.0067 | 0.9933 | 1.0000 | 0.0000 | 0.0264 | 0.9736 | 1.0000 | 0.0000 |
butyl laurate | 106-18-3 | Yes | 0.0035 | 0.9965 | 1.0000 | 0.0000 | 0.0182 | 0.9818 | 1.0000 | 0.0000 |
diethyl phthalate | 84-66-2 | Yes | 0.0092 | 0.9908 | 0.9993 | 0.0007 | 0.0519 | 0.9481 | 0.9972 | 0.0028 |
ethyl succinate | 123-25-1 | Yes | 0.0189 | 0.9811 | 0.9949 | 0.0051 | 0.0782 | 0.9218 | 0.9920 | 0.0080 |
diisobutyl succinate | 925-06-4 | Yes | 0.0133 | 0.9867 | 0.9998 | 0.0002 | 0.0453 | 0.9547 | 0.9995 | 0.0005 |
dimethyl adipate | 627-93-0 | Yes | 0.0189 | 0.9811 | 0.9949 | 0.0051 | 0.0782 | 0.9218 | 0.9920 | 0.0080 |
dimethyl phthalate | 131-11-3 | Yes | 0.0133 | 0.9867 | 0.9998 | 0.0002 | 0.0453 | 0.9547 | 0.9995 | 0.0005 |
dimethyl succinate | 106-65-0 | Yes | 0.0352 | 0.9648 | 0.9631 | 0.0369 | 0.1453 | 0.8547 | 0.9516 | 0.0484 |
methyl laurate | 111-82-0 | Yes | 0.0043 | 0.9957 | 1.0000 | 0.0000 | 0.0234 | 0.9766 | 1.0000 | 0.0000 |
ethyl laurate | 106-33-2 | Yes | 0.0041 | 0.9959 | 1.0000 | 0.0000 | 0.0213 | 0.9787 | 1.0000 | 0.0000 |
methyl myristate | 124-10-7 | Yes | 0.0032 | 0.9968 | 1.0000 | 0.0000 | 0.0193 | 0.9807 | 1.0000 | 0.0000 |
ethyl myristate | 124-06-1 | Yes | 0.0032 | 0.9968 | 1.0000 | 0.0000 | 0.0181 | 0.9819 | 1.0000 | 0.0000 |
| Substance                        | CAS     | Activity | Relative Activity |
|---------------------------------|---------|----------|-------------------|
| ethyl linoleate                 | 544-35-4| Yes      | 0.0023            |
| isopropyl myristate             | 110-27-0| Yes      | 0.0296            |
| benzoic acid phenylmethyl ester| 118-58-1| Yes      | 0.0034            |
| ricinoleic acid methyl ester    | 141-24-2| Yes      | 0.0110            |
| dimethyl glutarate              | 1119-40-0| Yes     | 0.0379            |
| diisobutyl glutarate            | 71195-64-7| Yes     | 0.0092            |
| methyl abietate                 | 127-25-3| Yes      | 0.0027            |
| methyl palmitate                | 112-39-0| Yes      | 0.0024            |
| isopropyl palmitate             | 142-91-6| Yes      | 0.0021            |
| methyl stearate                 | 112-61-5| Yes      | 0.0019            |
| methyl linoleate                | 112-63-0| Yes      | 0.0016            |
| methyl linolenate               | 301-00-8| Yes      | 0.0026            |
| ethyl oleate                    | 111-62-6| Yes      | 0.0021            |
| methyl oleate                   | 112-62-9| Yes      | 0.0021            |
| octadecanoic acid butyrate      | 123-95-5| Yes      | 0.0017            |
| dihydroterpinyl acetate         | 58985-18-5| Yes    | 0.0088            |
| glycerol triacetate             | 102-76-1| Yes      | 0.0032            |
| triethyl citrate                | 77-93-0 | Yes      | 0.0127            |
| y-Valerolactone                 | 108-29-2| No       |                   |
| 2-ethylhexyl lactate            | 6283-86-9| Yes     | 0.0180            |
| Ethyl lactate                   | 97-64-3 | Yes      | 0.1304            |
| 1,2-ethanediol diacetate        | 111-55-7| Yes      | 0.0680            |
| 4-methyl-2-pentyl acetate       | 108-84-9| Yes      | 0.0177            |
| 2-ethylhexyl acetate            | 103-09-3| Yes      | 0.0117            |
| Ketones                         |         |          |                   |
| acetone                         | 67-64-1 | No       |                   |
| butanone                        | 78-93-3 | No       |                   |
| methyl isobutyl ketone          | 108-10-1| Yes      | 0.2315            |
| cyclopentanone                  | 120-92-3| Yes      | 0.1275            |
| cyclohexanone                   | 108-94-1| Yes      | 0.1098            |
| Organic acids                   |         |          |                   |
| formic acid                     | 64-18-6 | No       |                   |
| acetic acid                     | 64-19-7 | No       |                   |
| propionic acid                  | 79-09-4 | No       |                   |
| hydroacrylic acid               | 503-66-2| No       |                   |
| Chemical Name          | CAS Number | Reaction | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
|------------------------|------------|----------|--------|--------|--------|--------|--------|--------|
| lactic acid            | 50-21-5    | No       |        |        |        |        |        |        |
| cis-9-octadecenoic acid| 112-80-1   | Yes      | 0.0204 | 0.9796 | 1.0000 | 0.0000 | 0.0324 | 0.9676 |
| ricinoleic acid        | 141-22-0   | Yes      | 0.0254 | 0.9746 | 1.0000 | 0.0000 | 0.0400 | 0.9600 |
| methanesulfonic acid   | 75-75-2    | No       |        |        |        |        |        |        |
| dimethyl ether         | 111109-77-4| No       |        |        |        |        |        |        |
| 2-methoxyethanol       | 109-86-4   | No       |        |        |        |        |        |        |
| dioxolane              | 646-06-0   | No       |        |        |        |        |        |        |
| dimethoxy methane      | 109-87-5   | Not at all temperatures |        |        |        |        |        |        |
| tetrahydrofuran        | 109-99-9   | Yes      | 0.3861 | 0.6139 | 0.7770 | 0.2230 | 0.3022 | 0.6978 |
| diethyl ether          | 60-29-7    | Yes      | 0.1196 | 0.8804 | 0.9867 | 0.0133 | 0.1076 | 0.8924 |
| dioxane                | 123-91-1   | No       |        |        |        |        |        |        |
| 1,2-dimethoxyethane    | 110-71-4   | Not at all temperatures |        |        |        |        |        |        |
| 2-methyltetrahydrofuran| 96-47-9    | Yes      | 0.2428 | 0.7572 | 0.9649 | 0.0351 | 0.1489 | 0.8511 |
| methyl t-butylether    | 1634-04-4  | Yes      | 0.1493 | 0.8507 | 0.9880 | 0.0120 | 0.1038 | 0.8962 |
| diethoxymethane        | 462-95-3   | Yes      | 0.0839 | 0.9161 | 0.9847 | 0.0153 | 0.0951 | 0.9049 |
| cyclopentyl methyl ether| 5614-37-9 | Yes      | 0.0482 | 0.9518 | 0.9953 | 0.0047 | 0.0636 | 0.9364 |
| diisopropyl ether      | 108-20-3   | Yes      | 0.0754 | 0.9246 | 0.9979 | 0.0021 | 0.0646 | 0.9354 |
| methyl tert-amyl ether | 994-05-8   | Yes      | 0.0572 | 0.9428 | 0.9970 | 0.0030 | 0.0596 | 0.9404 |
| 2-ethoxy-2-methyl-propane| 637-92-3 | Yes      | 0.0661 | 0.9339 | 0.9975 | 0.0025 | 0.0615 | 0.9385 |
| 1,1,3-trimethoxypropane| 14315-97-0| Yes      | 0.1124 | 0.8876 | 0.9593 | 0.0407 | 0.1089 | 0.8911 |
| dipropyleneglycol      | 25265-71-8| Not at all temperatures |        |        |        |        |        |        |
| diglyme                | 111-96-6   | Not at all temperatures |        |        |        |        |        |        |
| anisole                | 100-66-3   | Yes      | 0.0029 | 0.9971 | 0.9984 | 0.0016 | 0.0502 | 0.9498 |
| dimethyl isosorbide    | 5306-85-4  | Not at all temperatures |        |        |        |        |        |        |
| 1,4-cineol             | 470-67-7   | Yes      | 0.0267 | 0.9733 | 0.9995 | 0.0005 | 0.0366 | 0.9634 |
| 1,8-cineol             | 470-82-6   | Yes      | 0.0554 | 0.9446 | 0.9990 | 0.0010 | 0.0456 | 0.9544 |
| PEO                    | 25322-68-3 | Yes      | 0.1870 | 0.8130 | 0.8906 | 0.1094 | 0.1448 | 0.8552 |

**Organic carbonates**

| Chemical Name          | CAS Number | Reaction | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
|------------------------|------------|----------|--------|--------|--------|--------|--------|--------|
| dimethyl carbonate     | 616-38-6   | Yes      | 0.0626 | 0.9374 | 0.8895 | 0.1105 | 0.2869 | 0.7131 |
| diethyl carbonate      | 105-58-8   | Yes      | 0.0274 | 0.9726 | 0.9834 | 0.0166 | 0.1079 | 0.8921 |
| propylene carbonate    | 108-32-7   | Not at all temperatures |        |        |        |        |        |        |
| Compound                    | CAS号  | 溶解性  | 0.0612 | 0.9388 | 0.9176 | 0.0824 | 0.2940 | 0.7060 | 0.8116 | 0.1884 |
|-----------------------------|--------|---------|--------|--------|--------|--------|--------|--------|--------|--------|
| butylene carbonate         | 4437-85-8 | Yes |        |        |        |        |        |        |        |        |
| glycerol carbonate         | 931-40-8  | No  |        |        |        |        |        |        |        |        |

**Dipolar aprotic**

| Compound                    | CAS号  | 溶解性  | 0.0612 | 0.9388 | 0.9176 | 0.0824 | 0.2940 | 0.7060 | 0.8116 | 0.1884 |
|-----------------------------|--------|---------|--------|--------|--------|--------|--------|--------|--------|--------|
| nitromethane                 | 75-52-5 | No  | 0.0368 | 0.9632 | 0.9485 | 0.0515 |        |        |        |        |
| acetonitrile                 | 75-05-8  | No  |        |        |        |        |        |        |        |        |
| dimethylformamide           | 68-12-2  | No  |        |        |        |        |        |        |        |        |
| n,n-dimethylacetamide       | 127-19-5 | No  |        |        |        |        |        |        |        |        |
| n,n-dimethyloctanamide      | 1118-92-9 | Yes | 0.1842 | 0.8158 | 0.9976 | 0.0024 | 0.1003 | 0.8997 | 0.9982 | 0.0018 |
| dimethylsulfoxide           | 67-68-5  | No  |        |        |        |        |        |        |        |        |
| sulfolane                   | 126-33-0  | No  |        |        |        |        |        |        |        |        |
| hexamethylphosphoramide     | 680-31-9 | No  |        |        |        |        |        |        |        |        |

**Aromatics**

| Compound                    | CAS号  | 溶解性  | 0.0612 | 0.9388 | 0.9176 | 0.0824 | 0.2940 | 0.7060 | 0.8116 | 0.1884 |
|-----------------------------|--------|---------|--------|--------|--------|--------|--------|--------|--------|--------|
| benzene                     | 71-43-2  | Yes | 0.0013 | 0.9987 | 0.9978 | 0.0022 | 0.0480 | 0.9520 | 0.9857 | 0.0143 |
| toluene                     | 108-88-3 | Yes | 0.0011 | 0.9989 | 0.9985 | 0.0015 | 0.0455 | 0.9545 | 0.9901 | 0.0099 |
| 1,2-dimethylbenzene         | 95-47-6  | Yes | 0.0009 | 0.9991 | 0.9993 | 0.0007 | 0.0347 | 0.9653 | 0.9942 | 0.0058 |
| 1,3-dimethylbenzene         | 108-38-3 | Yes | 0.0007 | 0.9993 | 0.9997 | 0.0003 | 0.0285 | 0.9715 | 0.9969 | 0.0031 |
| 1,4-dimethylbenzene         | 106-42-3 | Yes | 0.0007 | 0.9993 | 0.9998 | 0.0002 | 0.0271 | 0.9729 | 0.9975 | 0.0025 |
| 1-methyl-4-isopropylbenzene | 99-87-6  | Yes | 0.0007 | 0.9993 | 0.9997 | 0.0003 | 0.0270 | 0.9730 | 0.9975 | 0.0025 |

**Hydrocarbons**

| Compound                    | CAS号  | 溶解性  | 0.0612 | 0.9388 | 0.9176 | 0.0824 | 0.2940 | 0.7060 | 0.8116 | 0.1884 |
|-----------------------------|--------|---------|--------|--------|--------|--------|--------|--------|--------|--------|
| pentane                     | 109-66-0 | Yes | 0.0002 | 0.9998 | 0.9999 | 0.0001 | 0.0168 | 0.9832 | 0.9991 | 0.0009 |
| hexane                      | 110-54-3 | Yes | 0.0002 | 0.9998 | 1.0000 | 0.0000 | 0.0144 | 0.9856 | 0.9996 | 0.0004 |
| cyclohexane                 | 110-82-7 | Yes | 0.0002 | 0.9998 | 0.9998 | 0.0002 | 0.0154 | 0.9846 | 0.9982 | 0.0018 |
| n-heptane                   | 142-82-5 | Yes | 0.0002 | 0.9998 | 1.0000 | 0.0000 | 0.0128 | 0.9872 | 0.9998 | 0.0002 |
| methylcyclohexane           | 108-67-2 | Yes | 0.0002 | 0.9998 | 0.9999 | 0.0001 | 0.0137 | 0.9863 | 0.9992 | 0.0008 |
| 2,2,4-trimethylpentane      | 540-84-1 | Yes | 0.0002 | 0.9998 | 1.0000 | 0.0000 | 0.0123 | 0.9877 | 0.9998 | 0.0002 |
| myrcene                     | 123-35-3 | Yes | 0.0004 | 0.9996 | 1.0000 | 0.0000 | 0.0183 | 0.9817 | 0.9997 | 0.0003 |
| limonene                    | 138-86-3 | Yes | 0.0004 | 0.9996 | 1.0000 | 0.0000 | 0.0166 | 0.9834 | 0.9996 | 0.0004 |
| β-pinene                    | 80-56-8  | Yes | 0.0002 | 0.9998 | 1.0000 | 0.0000 | 0.0130 | 0.9870 | 0.9996 | 0.0004 |
| β-pinene                    | 127-91-3 | Yes | 0.0003 | 0.9997 | 1.0000 | 0.0000 | 0.0145 | 0.9855 | 0.9995 | 0.0005 |
| terpinolene                 | 586-62-9  | Yes | 0.0004 | 0.9996 | 1.0000 | 0.0000 | 0.0161 | 0.9839 | 0.9997 | 0.0003 |
| (z)-beta-farnesene          | 28973-99-1 | Yes | 0.0003 | 0.9997 | 1.0000 | 0.0000 | 0.0128 | 0.9872 | 1.0000 | 0.0000 |

**Halogenated**

| Compound                    | CAS号  | 溶解性  | 0.0612 | 0.9388 | 0.9176 | 0.0824 | 0.2940 | 0.7060 | 0.8116 | 0.1884 |
|-----------------------------|--------|---------|--------|--------|--------|--------|--------|--------|--------|--------|
| chloroform                  | 67-66-3 | Yes | 0.0056 | 0.9944 | 0.9932 | 0.0068 | 0.0497 | 0.9503 | 0.9705 | 0.0295 |

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| Substance                        | CAS Number | Solubility | D1   | D2   | D3   | D4   | D5   | D6   | D7   |
|---------------------------------|------------|------------|------|------|------|------|------|------|------|
| dichloromethane                 | 75-09-2    | Yes        | 0.0068 | 0.9932 | 0.9716 | 0.0284 | 0.1193 | 0.8807 | 0.8741 | 0.1259 |
| Tetrachloromethane              | 56-23-5    | Yes        | 0.0002 | 0.9998 | 0.9996 | 0.0004 | 0.0104 | 0.9896 | 0.9966 | 0.0034 |
| cis,1,2-dichloroethene          | 156-59-2   | Yes        | 0.0027 | 0.9973 | 0.9921 | 0.0079 | 0.0565 | 0.9435 | 0.9609 | 0.0391 |
| 1,2-dichloroethene              | 107-06-2   | Yes        | 0.0031 | 0.9969 | 0.9898 | 0.0102 | 0.0821 | 0.9179 | 0.9317 | 0.0683 |
| chlorobenzene                   | 108-90-7   | Yes        | 0.0009 | 0.9991 | 0.9990 | 0.0010 | 0.0321 | 0.9679 | 0.9915 | 0.0085 |
| trifluoroacetic acid            | 76-05-1    | No         | 0.0006 | 0.9994 | 0.9993 | 0.0007 | 0.0231 | 0.9769 | 0.9944 | 0.0056 |
| trifluoromethyl benzene         | 98-08-8    | Yes        | 0.0000 | 1.0000 | 1.0000 | 0.0000 | 0.0025 | 0.9975 | 1.0000 | 0.0000 |
| Bases                           |            |            |      |      |      |      |      |      |      |
| 2-pyrrolidone                   | 616-45-5   | No         | 0.3555 | 0.6445 | 0.8866 | 0.1134 | 0.3246 | 0.6754 | 0.8645 | 0.1355 |
| pyridine                        | 110-86-1   | Yes        | 0.0725 | 0.9275 | 0.9997 | 0.0003 | 0.0618 | 0.9382 | 0.9985 | 0.0015 |
| n-methyl-2-pyrrolidone          | 872-50-4   | No         | 0.4066 | 0.5934 | 0.9031 | 0.0969 |      |      |      |      |
| 1,3-dimethyl-2-imidazolidinone  | 80-73-9    | No         | 0.4101 | 0.5899 | 0.8690 | 0.1310 |      |      |      |      |
| tetramethylurea                 | 632-22-4   | Not at all temperatures |      |      |      |      |      |      |      |      |
| N,N’-Dimethylpropyleneurea      | 7226-23-5  | Not at all temperatures |      |      |      |      |      |      |      |      |
| 2,4,6-collidine                 | 108-75-6   | Yes        | 0.1197 | 0.8803 | 0.9963 | 0.0037 | 0.0928 | 0.9072 | 0.9935 | 0.0065 |
| 1,2-dimethyl-3-nitrobenzene     | 83-41-0    | Yes        | 0.0023 | 0.9977 | 0.9996 | 0.0004 | 0.0406 | 0.9594 | 0.9949 | 0.0051 |
| 1,3-dimethyl-2-nitrobenzene     | 81-20-9    | Yes        | 0.0016 | 0.9884 | 0.9997 | 0.0003 | 0.0360 | 0.9640 | 0.9955 | 0.0045 |
| 1,4-dimethyl-2-nitrobenzene     | 89-58-7    | Yes        | 0.0025 | 0.9975 | 0.9996 | 0.0004 | 0.0392 | 0.9608 | 0.9958 | 0.0042 |
| methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate | 1174627-68-9 | Not at all temperatures |      |      |      |      |      |      |      |      |
| Other                           |            |            |      |      |      |      |      |      |      |      |
| decamethylcyclopentasiloxane    | 541-02-6   | Yes        | 0.0007 | 0.9993 | 1.0000 | 0.0000 | 0.0091 | 0.9909 | 1.0000 | 0.0000 |
| carbon disulfide                | 75-15-0    | Yes        | 0.0002 | 0.9998 | 0.9993 | 0.0007 | 0.0169 | 0.9831 | 0.9939 | 0.0061 |
Table S2. COSMO-RS: relative solubility (log$_{10}$(w$_{solub}$)) predictions and probability of solubility of 5-HMF and furfural at 298.15 and 423.15 K in solvents showing miscibility gap with water.

| Solvent                  | CAS   | log$_{10}$(w$_{solub}$) | Probability | log$_{10}$(w$_{solub}$) | Probability | log$_{10}$(w$_{solub}$) | Probability |
|--------------------------|-------|--------------------------|-------------|--------------------------|-------------|--------------------------|-------------|
| **Alcohols**             |       |                          |             |                          |             |                          |             |
| 1-butanol                | 71-36-3| -0.4731                  | 0.3364      | -0.2646                  | 0.5437      | -0.581                   | 0.2624      | -0.2269 | 0.593 |
| 2-butanol                | 78-92-2| -0.4322                  | 0.3697      | -0.2723                  | 0.5342      | -0.553                   | 0.2799      | -0.2238 | 0.5973 |
| isobutanol               | 78-83-1| -0.4852                  | 0.3272      | -0.2778                  | 0.5274      | -0.5416                  | 0.2873      | -0.2181 | 0.6052 |
| tert-butanol             | 75-85-0| -0.3636                  | 0.4329      | -0.25                   | 0.5624      | -0.5554                  | 0.2783      | -0.2241 | 0.5968 |
| 1-pentanol               | 71-41-0| -0.5714                  | 0.2683      | -0.3403                  | 0.4567      | -0.6146                  | 0.2429      | -0.2524 | 0.5592 |
| isopentanol              | 123-51-3| -0.555                   | 0.2786      | -0.3284                  | 0.4695      | -0.5921                  | 0.2558      | -0.2415 | 0.5735 |
| 2-methyl-2-butanol       | 75-85-4| -0.5464                  | 0.2842      | -0.3685                  | 0.4281      | -0.5843                  | 0.2604      | -0.2539 | 0.5573 |
| tetrahydrofurfuryl alcohol| 97-99-4| 0.0                      | 1.0         | -0.0799                  | 0.832       | -0.2784                  | 0.5267      | -0.1179 | 0.7623 |
| furfuryl alcohol         | 98-00-0| 0.0                      | 1.0         | -0.0033                  | 0.9924      | 0.0                      | 1.0         | 0.0     | 0.0 |
| 1-hexanol                | 111-27-3| -0.658                   | 0.2198      | -0.3992                  | 0.3968      | -0.6437                  | 0.2271      | -0.2708 | 0.5361 |
| 3-methoxy-3-methylbutanol| 56539-86-3| 0.0                     | 1.0         | -0.0762                  | 0.8392      | -0.221                   | 0.6011      | -0.1173 | 0.7633 |
| 1-heptanol               | 111-70-6| -0.7271                  | 0.1875      | -0.452                   | 0.3532      | -0.669                   | 0.2143      | -0.2896 | 0.5134 |
| benzyl alcohol           | 100-51-6| -0.0952                  | 0.8031      | -0.0816                  | 0.8287      | -0.0285                  | 0.9365      | 0.0     | 1.0 |
| 1-octanol                | 111-87-5| -0.793                   | 0.1611      | -0.4967                  | 0.3187      | -0.6912                  | 0.2036      | -0.3038 | 0.4968 |
| 1-decanol                | 112-30-1| -0.896                   | 0.1271      | -0.5623                  | 0.274       | -0.7269                  | 0.1876      | -0.3247 | 0.4734 |
| dihydromycroenol         | 53219-21-9| -0.69                    | 0.2042      | -0.4961                  | 0.3191      | -0.5477                  | 0.2833      | -0.2514 | 0.5605 |
| geraniol                 | 106-24-1| -0.4896                  | 0.3239      | -0.3487                  | 0.4481      | -0.4226                  | 0.3779      | -0.1682 | 0.6789 |
| dihydro terpineol        | 58985-02-7| -0.7547                  | 0.1759      | -0.5351                  | 0.2917      | -0.6977                  | 0.2006      | -0.3198 | 0.4788 |
| β-terpineol              | 98-55-5| -0.6765                  | 0.2106      | -0.4794                  | 0.3316      | -0.5263                  | 0.2976      | -0.2456 | 0.558 |
| nopol                    | 138-87-4| -0.6502                  | 0.2238      | -0.4573                  | 0.3489      | -0.4814                  | 0.3301      | -0.226   | 0.5943 |
| oleyl alcohol            | 143-28-2| -1.0488                  | 0.0694      | -0.6512                  | 0.2233      | -0.6763                  | 0.2107      | -0.3032 | 0.4976 |
| **Esters**               |       |                          |             |                          |             |                          |             |
| methyl acetate           | 79-20-9| -0.0774                  | 0.8367      | -0.0522                  | 0.8868      | -0.0002                  | 0.9996      | -0.015  | 0.966 |
| ethyl acetate            | 141-78-6| -0.2058                  | 0.6225      | -0.1667                  | 0.6812      | -0.086                   | 0.8203      | -0.073  | 0.8452 |
| isopropyl acetate        | 108-21-4| -0.3807                  | 0.4162      | -0.2842                  | 0.5198      | -0.1915                  | 0.6435      | -0.1328 | 0.7365 |
| n-propyl acetate         | 109-60-4| -0.3867                  | 0.4105      | -0.2828                  | 0.5214      | -0.1883                  | 0.6482      | -0.1315 | 0.7387 |
| Compound                        | Number  | R   | S   | T   | U   | V   | X   |
|--------------------------------|---------|-----|-----|-----|-----|-----|-----|
| n-butyl acetate                | 123-86-4| -0.5161 | 0.3047 | -0.3624 | 0.4341 | -0.2845 | 0.5439 | -0.1716 | 0.6735 |
| n-pentyl acetate               | 628-63-7| -0.6367 | 0.2308 | -0.4312 | 0.3705 | -0.331 | 0.4666 | -0.2052 | 0.6234 |
| isoamyl acetate                | 123-92-2| -0.5858 | 0.2596 | -0.4043 | 0.3942 | -0.3057 | 0.4947 | -0.1917 | 0.6432 |
| geranyl acetate                | 105-87-3| -0.9308 | 0.1173 | -0.5313 | 0.2943 | -0.383 | 0.414 | -0.1959 | 0.6369 |
| adipic acid diethyl ester      | 141-28-6| -0.3738 | 0.4228 | -0.2299 | 0.5889 | -0.1343 | 0.734 | -0.0716 | 0.8479 |
| ethyl palmitate                | 628-97-7| -1.4339 | 0.0368 | -0.819 | 0.1517 | -0.7317 | 0.1855 | -0.3727 | 0.4239 |
| acetic anhydride               | 108-24-7| -0.4143 | 0.3852 | -0.1075 | 0.7807 | -0.0387 | 0.9148 | -0.0155 | 0.9649 |
| methyl propionate              | 554-12-1| -0.3412 | 0.4558 | -0.216 | 0.6082 | -0.1308 | 0.74 | -0.0913 | 0.8105 |
| isobutyl acetate               | 110-19-0| -0.5187 | 0.3029 | -0.3643 | 0.4323 | -0.2674 | 0.5403 | -0.1745 | 0.6691 |
| dibutyl sebacate               | 109-43-3| -0.7914 | 0.1617 | -0.4682 | 0.3402 | -0.3731 | 0.4236 | -0.1805 | 0.6599 |
| diethyl phthalate              | 84-86-2| -0.5796 | 0.2633 | -0.2584 | 0.5516 | -0.111 | 0.7745 | -0.0349 | 0.9229 |
| ethyl succinate                | 123-25-1| -0.48 | 0.3311 | -0.233 | 0.5848 | -0.1334 | 0.7356 | -0.0658 | 0.8594 |
| diisobutyl succinate           | 925-06-4| -0.5946 | 0.2543 | -0.3571 | 0.4394 | -0.2603 | 0.5492 | -0.1341 | 0.7344 |
| dimethyl adipate               | 627-93-0| -0.2816 | 0.5228 | -0.1467 | 0.7133 | -0.069 | 0.8531 | -0.0336 | 0.9255 |
| dimethyl phthalate             | 131-11-3| -0.4882 | 0.3249 | -0.1846 | 0.6538 | -0.0487 | 0.8939 | -0.003 | 0.9931 |
| dimethyl succinate             | 106-65-0| -0.3305 | 0.4672 | -0.1236 | 0.7524 | -0.0573 | 0.8763 | -0.0219 | 0.9508 |
| methyl laurate                 | 111-82-0| -1.2205 | 0.0602 | -0.7101 | 0.1949 | -0.6122 | 0.2442 | -0.3265 | 0.4715 |
| ethyl laurate                  | 106-33-2| -1.2401 | 0.0575 | -0.7343 | 0.1844 | -0.6419 | 0.2281 | -0.3418 | 0.4552 |
| butyl laurate                  | 106-18-3| -1.3149 | 0.0484 | -0.7785 | 0.1665 | -0.6989 | 0.2 | -0.3645 | 0.432 |
| methyl myristate               | 124-10-7| -1.3228 | 0.0476 | -0.7563 | 0.1753 | -0.6631 | 0.2172 | -0.3455 | 0.4513 |
| ethyl myristate                | 124-06-1| -1.3199 | 0.0479 | -0.771 | 0.1694 | -0.6863 | 0.2059 | -0.3565 | 0.44 |
| ethyl linoleate                | 544-35-4| -1.2614 | 0.0548 | -0.6825 | 0.2077 | -0.5688 | 0.2699 | -0.2652 | 0.543 |
| isopropyl myristate            | 110-27-0| -1.4063 | 0.0392 | -0.8161 | 0.1527 | -0.7374 | 0.1831 | -0.3789 | 0.418 |
| benzoic acid phenylmethylster  | 118-58-1| -0.912 | 0.1225 | -0.408 | 0.3909 | -0.1858 | 0.6519 | -0.066 | 0.859 |
| ricinoleic acid methylster     | 141-24-2| -0.6902 | 0.2041 | -0.5025 | 0.3144 | -0.4295 | 0.372 | -0.2052 | 0.6235 |
| dimethyl glutarate             | 1119-40-0| -0.287 | 0.5164 | -0.1368 | 0.7298 | -0.0565 | 0.8781 | -0.0271 | 0.9394 |
| diisobutyl glutarate           | 71195-64-7| -0.6111 | 0.2449 | -0.3609 | 0.4356 | -0.2601 | 0.5495 | -0.131 | 0.7396 |
| methyl abietate                | 127-25-3| -1.414 | 0.0386 | -0.7334 | 0.1847 | -0.6153 | 0.2425 | -0.2884 | 0.5148 |
| methyl palmitate               | 112-39-0| -1.4097 | 0.0389 | -0.7933 | 0.161 | -0.7031 | 0.1981 | -0.3578 | 0.4387 |
| isopropyl palmitate            | 142-91-6| -1.4914 | 0.0323 | -0.8473 | 0.1421 | -0.7726 | 0.1888 | -0.389 | 0.4083 |
| methyl stearate                | 112-61-8| -1.4994 | 0.0317 | -0.8284 | 0.1485 | -0.7425 | 0.1809 | -0.371 | 0.4256 |
| methyl linoleate               | 112-63-0| -1.2524 | 0.0559 | -0.672 | 0.2128 | -0.5645 | 0.2841 | -0.2573 | 0.5529 |
| methyl linolenate              | 301-00-8| -1.1295 | 0.0742 | -0.5863 | 0.2592 | -0.4418 | 0.3616 | -0.1953 | 0.6378 |
| ethyl oleate                   | 111-62-6| -1.3775 | 0.0419 | -0.7664 | 0.1713 | -0.669 | 0.2143 | -0.3255 | 0.4726 |
| methyl oleate                  | 112-62-9| -1.3705 | 0.0426 | -0.746 | 0.1795 | -0.6382 | 0.23 | -0.3118 | 0.4878 |
| Chemical Name                  | CAS Number | K    | n    | α    | ω    | ρ    | ω/K   | ω/n   |
|-------------------------------|------------|------|------|-----|-----|-----|-------|-------|
| octadecanoic acid butylester  | 123-95-5   | -1.545 | 0.0285 | -0.8682 | 0.1355 | -0.7966 | 0.1597 | -0.3917 | 0.4058 |
| dihydroterpinyl acetate       | 58985-18-5 | -0.9868 | 0.1031 | -0.6519 | 0.2229 | -0.5647 | 0.2725 | -0.3148 | 0.4844 |
| glycerol triacetate           | 102-76-1   | -0.2264 | 0.9937 | -0.0776 | 0.8364 | -0.0023 | 0.9947 | 0.0 | 1.0 |
| triethyl citrate              | 77-93-0    | -0.4219 | 0.3785 | -0.1951 | 0.6381 | -0.0866 | 0.8155 | -0.0183 | 0.9588 |
| 2-ethylhexyl lactate          | 6283-86-9  | -0.6624 | 0.2176 | -0.5078 | 0.3106 | -0.4351 | 0.3672 | -0.236 | 0.5808 |
| Ethyl lactate                 | 97-64-3    | -0.1275 | 0.7456 | -0.1682 | 0.679 | -0.1543 | 0.7009 | -0.083 | 0.8261 |
| 1,2-ethanediol diacetate      | 111-55-7   | -0.1622 | 0.6883 | -0.0697 | 0.8518 | -0.0101 | 0.9769 | -0.0045 | 0.9896 |
| 4-methyl-2-pentylacetate      | 108-84-9   | -0.7512 | 0.1773 | -0.5006 | 0.3158 | -0.3976 | 0.4003 | -0.2379 | 0.5782 |
| 2-ethylhexyl acetate          | 103-09-3   | -0.8762 | 0.133 | -0.5756 | 0.2657 | -0.4743 | 0.3355 | -0.2743 | 0.5317 |

### Ketones

| Chemical Name                  | CAS Number | K    | n    | α    | ω    | ρ    | ω/K   | ω/n   |
|-------------------------------|------------|------|------|-----|-----|-----|-------|-------|
| methyl isobutyl ketone        | 108-10-1   | -0.2979 | 0.5037 | -0.2895 | 0.5135 | -0.2285 | 0.5909 | -0.157 | 0.6967 |
| cyclopentanone                | 120-92-3   | 0.0 | 1.0 | -0.0442 | 0.9033 | -0.0166 | 0.9624 | -0.0429 | 0.9059 |
| cyclohexanone                 | 108-94-1   | 0.0 | 1.0 | -0.1172 | 0.7635 | -0.0795 | 0.8327 | -0.0832 | 0.8256 |

### Organic acids

| Chemical Name                  | CAS Number | K    | n    | α    | ω    | ρ    | ω/K   | ω/n   |
|-------------------------------|------------|------|------|-----|-----|-----|-------|-------|
| cis-9-octadecenoic acid       | 112-80-1   | -0.5847 | 0.2602 | -0.471 | 0.3381 | -0.1483 | 0.7107 | -0.147 | 0.7128 |
| ricinoleic acid               | 141-22-0   | -0.6711 | 0.2133 | -0.3735 | 0.4231 | -0.3812 | 0.4158 | -0.1373 | 0.729 |

### Ethers

| Chemical Name                  | CAS Number | K    | n    | α    | ω    | ρ    | ω/K   | ω/n   |
|-------------------------------|------------|------|------|-----|-----|-----|-------|-------|
| dimethoxymethane              | 109-87-5   | -0.0185 | 0.9582 | -0.1421 | 0.7209 | -0.0885 | 0.8157 | -0.0828 | 0.8264 |
| tetrahydrofuran               | 109-99-9   | 0.0 | 1.0 | -0.0967 | 0.8004 | -0.0795 | 0.8328 | -0.1205 | 0.7577 |
| diethyl ether                 | 60-29-7    | -0.3843 | 0.4128 | -0.4881 | 0.325 | -0.4311 | 0.3706 | -0.2961 | 0.5057 |
| 1,2-dimethoxyethane           | 110-71-4   | 0.0 | 1.0 | -0.0806 | 0.8306 | -0.0391 | 0.9139 | -0.0749 | 0.8416 |
| 2-methyltetrahydrofuran       | 96-47-9    | 0.0 | 1.0 | -0.3053 | 0.4951 | -0.2714 | 0.5354 | -0.2229 | 0.5986 |
| methyl tert-butyl ether       | 1634-04-4  | -0.1856 | 0.6522 | -0.4622 | 0.345 | -0.4146 | 0.385 | -0.2996 | 0.5017 |
| diethoxymethane               | 462-95-3   | -0.4001 | 0.398 | -0.405 | 0.3935 | -0.3336 | 0.4639 | -0.2224 | 0.5992 |
| cyclopentyl methyl ether      | 5614-37-9  | -0.6602 | 0.2187 | -0.623 | 0.2382 | -0.5673 | 0.2708 | -0.3538 | 0.4428 |
| diisopropyl ether             | 108-20-3   | -0.4097 | 0.3893 | -0.6117 | 0.2445 | -0.5699 | 0.2692 | -0.3736 | 0.423 |
| methyl tert-amyl ether        | 994-05-8   | -0.5773 | 0.2647 | -0.6564 | 0.2206 | -0.5954 | 0.2539 | -0.3806 | 0.4163 |
| 2-ethoxy-2-methyl-propane     | 637-92-3   | -0.5074 | 0.3109 | -0.6411 | 0.2285 | -0.5892 | 0.2575 | -0.3809 | 0.416 |
| 1,1,3-trimethoxypropane       | 14315-97-0 | -0.1968 | 0.6356 | -0.2615 | 0.5476 | -0.199 | 0.6323 | -0.133 | 0.7362 |
| dipropylene glycol            | 25265-71-8 | 0.0 | 1.0 | -0.0719 | 0.8474 | -0.3037 | 0.4969 | -0.1138 | 0.7694 |
| diglyme                       | 111-96-6   | 0.0 | 1.0 | -0.1113 | 0.774 | -0.0489 | 0.8935 | -0.0749 | 0.8416 |
| anisole                       | 100-66-3   | -1.2154 | 0.0609 | -0.4966 | 0.3187 | -0.2701 | 0.5369 | -0.1259 | 0.7483 |
| dimethyl isosorbide           | 5306-85-4  | 0.0 | 1.0 | -0.078 | 0.8356 | -0.0515 | 0.8882 | -0.0345 | 0.9237 |
| 1,4-cineol                    | 470-67-7   | -0.7561 | 0.1753 | -0.7227 | 0.1894 | -0.6797 | 0.2091 | -0.4058 | 0.3928 |
| 1,8-cineol                    | 470-82-6   | -0.4035 | 0.3949 | -0.6287 | 0.2351 | -0.6111 | 0.2448 | -0.3852 | 0.4119 |
|                |    |     |    |     |     |     |     |     |
|----------------|----|-----|----|-----|-----|-----|-----|-----|
| **PEO**        | 25322-68-3 | -0.1322 | 0.7376 | -0.2292 | 0.59 | -0.1906 | 0.6448 | -0.1379 | 0.7279 |
| **Organic carbonates** |    |     |    |     |     |     |     |     |
| dimethyl carbonate | 616-38-6 | -0.3325 | 0.465 | -0.1033 | 0.7882 | -0.0465 | 0.8984 | -0.0216 | 0.9514 |
| diethyl carbonate | 105-58-8 | -0.5135 | 0.3066 | -0.256 | 0.5546 | -0.1595 | 0.6926 | -0.0944 | 0.8047 |
| propylene carbonate | 108-32-7 | -0.2537 | 0.5576 | -0.0534 | 0.8842 | -0.0925 | 0.8082 | -0.0513 | 0.8886 |
| butylene carbonate | 4437-85-8 | -0.2913 | 0.5114 | -0.0861 | 0.8201 | -0.0784 | 0.8349 | -0.0353 | 0.9219 |
| **Dipolar aprotic** |    |     |    |     |     |     |     |     |
| nitromethane | 75-52-5 | -0.6006 | 0.2509 | -0.0918 | 0.8095 | -0.0941 | 0.8052 | -0.0309 | 0.9314 |
| n,n-dimethyloctanamide | 1118-92-9 | 0.0 | 1.0 | -0.1513 | 0.7059 | -0.1295 | 0.7422 | -0.1276 | 0.7455 |
| hexamethylphosphoramide | 680-31-9 | 0.0 | 1.0 | 0.0 | 1.0 | 0.0 | 1.0 | 0.0 | 1.0 |
| **Aromatics** |    |     |    |     |     |     |     |     |
| benzene | 71-43-2 | -1.6821 | 0.0208 | -0.6352 | 0.2316 | -0.3875 | 0.4097 | -0.1847 | 0.6536 |
| toluene | 108-83-3 | -1.8617 | 0.0138 | -0.7377 | 0.1829 | -0.5083 | 0.3103 | -0.25 | 0.5624 |
| 1,2-dimethylbenzene | 95-47-6 | -1.948 | 0.0113 | -0.7859 | 0.1637 | -0.5663 | 0.2715 | -0.2793 | 0.5257 |
| 1,3-dimethylbenzene | 108-38-3 | -2.0029 | 0.0099 | -0.8154 | 0.153 | -0.605 | 0.2483 | -0.3002 | 0.501 |
| 1,4-dimethylbenzene | 106-42-3 | -2.0038 | 0.0099 | -0.8162 | 0.1527 | -0.6044 | 0.2487 | -0.3 | 0.5011 |
| 1-methyl-4-isopropylbenzene | 99-87-6 | -2.1808 | 0.0066 | -0.9107 | 0.1228 | -0.7206 | 0.1903 | -0.3568 | 0.4397 |
| **Hydrocarbons** |    |     |    |     |     |     |     |     |
| pentane | 109-66-0 | -3.2061 | 0.0006 | -1.4794 | 0.0332 | -1.4491 | 0.0356 | -0.7709 | 0.1695 |
| hexane | 110-54-3 | -3.2048 | 0.0006 | -1.4773 | 0.0333 | -1.4481 | 0.0356 | -0.7668 | 0.1711 |
| cyclohexane | 110-82-7 | -3.2057 | 0.0006 | -1.4669 | 0.0341 | -1.4644 | 0.0343 | -0.7713 | 0.1693 |
| n-heptane | 142-82-5 | -3.2 | 0.0006 | -1.4719 | 0.0337 | -1.4431 | 0.036 | -0.7596 | 0.1739 |
| methycyclohexane | 108-87-2 | -3.1903 | 0.0006 | -1.4587 | 0.0348 | -1.4496 | 0.0355 | -0.7605 | 0.1736 |
| 2,2,4-trimethylpentane | 540-84-1 | -3.1423 | 0.0007 | -1.4383 | 0.0364 | -1.3983 | 0.04 | -0.7318 | 0.1854 |
| myrcene | 123-35-3 | -2.2055 | 0.0062 | -0.9831 | 0.1185 | -0.7319 | 0.1854 | -0.3681 | 0.4284 |
| limonene | 138-86-3 | -2.4049 | 0.0039 | -1.0439 | 0.0904 | -0.8961 | 0.127 | -0.4549 | 0.3508 |
| l-limonene | 80-56-8 | -2.77 | 0.0017 | -1.2339 | 0.0584 | -1.1348 | 0.0733 | -0.5821 | 0.2618 |
| β-pinene | 127-91-3 | -2.6724 | 0.0024 | -1.1704 | 0.0675 | -1.0645 | 0.0862 | -0.5475 | 0.2835 |
| terpinolene | 566-62-9 | -2.4266 | 0.0037 | -1.0542 | 0.0683 | -0.9074 | 0.1238 | -0.4589 | 0.3476 |
| (Z)-beta-farnesene | 28973-99-1 | -2.2256 | 0.0059 | -0.929 | 0.1178 | -0.7285 | 0.1868 | -0.3438 | 0.4531 |
| **Halogenated** |    |     |    |     |     |     |     |     |
| chloroform | 67-66-3 | -0.4951 | 0.3198 | -0.421 | 0.3793 | 0.0 | 1.0 | -0.0722 | 0.8469 |
| dichloromethane | 75-09-2 | -0.548 | 0.2831 | -0.1957 | 0.6372 | 0.0 | 1.0 | 0.0 | 1.0 |
| Compound                        | CAS       | Density | Viscosity | Refraction | Boiling Point | Melting Point |
|--------------------------------|-----------|---------|-----------|------------|---------------|---------------|
| Tetrachloromethane             | 56-23-5  | -2.901  | 0.0013    | -1.2997    | 0.0502        | -1.2291       |
| cis-1,2-dichloroethene         | 156-59-2 | -1.0092 | 0.0979    | -0.4395    | 0.3635        | 0.0           |
| 1,2-dichloroethane             | 107-06-2 | -1.0658 | 0.086     | -0.3468    | 0.45          | -0.0976       |
| Chlorobenzene                  | 108-90-7 | -1.6908 | 0.0204    | -0.6587    | 0.2194        | -0.385        |
| Trifluoromethyl benzene        | 98-08-8  | -1.8484 | 0.0142    | -0.7654    | 0.1716        | -0.5311       |
| Perfluorooctane                | 307-34-6 | -4.3214 | 0.0       | -2.0985    | 0.008         | -2.3649       |
| Pyridine                       | 110-86-1 | 0.0     | 1.0       | 0.0        | 1.0           | 0.0           |
| Triethylamine                  | 121-44-8 | 0.0     | 1.0       | -0.4571    | 0.349         | -0.6226       |
| Tetramethylurea                | 632-22-4 | 0.0     | 1.0       | 0.0        | 1.0           | 0.0           |
| N,N'-Dimethylpropyleneurea     | 7226-23-5| 0.0     | 1.0       | 0.0        | 1.0           | 0.0           |
| 2,4,6-collidine                | 108-75-8 | 0.0     | 1.0       | -0.1855    | 0.6524        | -0.144        |
| 1,2-dimethyl-3-nitrobenzene    | 83-41-0  | -1.2084 | 0.0619    | -0.4711    | 0.338         | -0.2587       |
| 1,3-dimethyl-2-nitrobenzene    | 81-20-9  | -1.3562 | 0.044     | -0.5206    | 0.3016        | -0.2977       |
| 1,4-dimethyl-2-nitrobenzene    | 89-58-7  | -1.2111 | 0.0615    | -0.49      | 0.3236        | -0.2842       |
| Methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate | 1174627-68-9 | 0.0 | 1.0 | 0.0 | 1.0 | 0.0 | 1.0 |
| Decamethylcyclopentasiloxane   | 541-02-6 | -1.816  | 0.0153    | -0.9354    | 0.116         | -0.7998       |
| Carbon disulfide               | 75-15-0  | -2.8726 | 0.0013    | -1.2191    | 0.0604        | -1.0347       |

**Base**

- **Tetrachloromethane**
- **Cis-1,2-dichloroethene**
- **1,2-dichloroethane**
- **Chlorobenzene**
- **Trifluoromethyl benzene**
- **Perfluorooctane**
- **Pyridine**
- **Triethylamine**
- **Tetramethylurea**
- **N,N'-Dimethylpropyleneurea**
- **2,4,6-collidine**
- **1,2-dimethyl-3-nitrobenzene**
- **1,3-dimethyl-2-nitrobenzene**
- **1,4-dimethyl-2-nitrobenzene**
- **Methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate**

**Other**

- **Decamethylcyclopentasiloxane**
- **Carbon disulfide**
Table S3. Distribution coefficients calculated from COSMO-RS predictions of the LLE \(\text{H}_2\text{O} + 5\text{-HMF} + \text{solvent}\) at 298.15 K and 423.15 K for feed compositions simulated from different initial substrate concentrations. Note: the results for a feed composition corresponding to an initial concentration of fructose of 1% wt. at 423.15 K are marked in green italic font for reference for the ranking of solvents. The results for MIBK are highlighted due to this solvent being the most commonly applied in experimental studies. – denotes non-existing LLE.

| Solvent                   | CAS    | \(C_{\text{fruc}}\) =1% wt. | \(C_{\text{fruc}}\) =5% wt. | \(C_{\text{fruc}}\) =10% wt. | \(C_{\text{fruc}}\) =25% wt. | \(C_{\text{fruc}}\) =50% wt. | \(C_{\text{fruc}}\) =1% wt. | \(C_{\text{fruc}}\) =5% wt. | \(C_{\text{fruc}}\) =10% wt. | \(C_{\text{fruc}}\) =25% wt. | \(C_{\text{fruc}}\) =50% wt. |
|---------------------------|--------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| **Alcohols**              |        |                               |                               |                               |                               |                               |                               |                               |                               |                               |                               |
| 1-butanol                 | 71-36-3| 2.48                           | 2.49                           | 2.49                           | 2.49                           | 3.45                           | 3.43                           | 3.40                           | 3.32                           | 3.12                           |
| 2-butanol                 | 78-92-2| 2.53                           | 2.53                           | 2.54                           | 2.54                           | 3.45                           | 3.44                           | 3.41                           | 3.34                           | 3.15                           |
| isobutanol                | 78-83-1| 2.52                           | 2.52                           | 2.52                           | 2.52                           | 3.42                           | 3.40                           | 3.38                           | 3.30                           | 3.11                           |
| tert-butanol              | 75-65-0| 2.56                           | 2.56                           | 2.56                           | 2.54                           | 3.31                           | 3.29                           | 3.27                           | 3.17                           | 2.96                           |
| tetrahydrofurfuryl alcohol| 97-99-4| -                              | -                              | -                              | -                              | 1.76                           | 1.73                           | 1.69                           | -                              | -                              |
| furfuryl alcohol          | 98-00-0| 4.80                           | 4.75                           | 4.69                           | 4.49                           | 4.10                           | 2.20                           | 2.17                           | 2.13                           | 1.95                           | 1.63                           |
| 3-methoxy-3-methylbutanol | 56539-66-3| 2.22                       | 2.21                           | 2.20                           | 2.17                           | 2.07                           | 3.24                           | 3.22                           | 3.19                           | 3.11                           | 2.92                           |
| benzyl alcohol            | 100-51-6| 4.05                           | 4.04                           | 4.02                           | 3.95                           | 3.80                           | 3.83                           | 3.80                           | 3.77                           | 3.65                           | 3.40                           |
| **Ester**                 |        |                               |                               |                               |                               |                               |                               |                               |                               |                               |                               |
| methyl acetate            | 79-20-9| -                              | -                              | -                              | -                              | 2.06                           | 2.02                           | 1.97                           | 1.79                           | -                              |
| ethyl acetate             | 141-78-6| 3.61                          | 3.59                           | 3.55                           | 3.43                           | 3.19                           | 3.84                           | 3.82                           | 3.78                           | 3.68                           | 3.44                           |
| isopropyl acetate         | 108-21-4| 2.52                           | 2.51                           | 2.51                           | 2.50                           | 2.49                           | 3.02                           | 3.02                           | 3.01                           | 3.00                           | 2.95                           |
| n-propyl acetate          | 109-60-4| 2.50                           | 2.50                           | 2.49                           | 2.49                           | 2.48                           | 3.04                           | 3.03                           | 3.03                           | 3.01                           | 2.96                           |
| adipic acid diethyl ester | 141-28-6| 1.18                           | 1.19                           | 1.19                           | 1.20                           | 1.23                           | 1.73                           | 1.73                           | 1.73                           | 1.73                           | 1.72                           |
| acrylic anhydride         | 108-24-7| 2.22                           | 2.25                           | 2.29                           | 2.40                           | 2.58                           | 3.05                           | 3.02                           | 2.99                           | 2.85                           | 2.55                           |
| methyl propionate         | 554-12-1| 3.11                           | 3.10                           | 3.10                           | 3.09                           | 3.04                           | 3.58                           | 3.67                           | 3.65                           | 3.58                           | 3.40                           |
| diethyl phthalate         | 84-66-2| 0.60                           | 0.61                           | 0.61                           | 0.63                           | 0.67                           | 1.47                           | 1.48                           | 1.48                           | 1.51                           | 1.54                           |
| ethyl succinate           | 123-25-1| 1.08                           | 1.09                           | 1.11                           | 1.15                           | 1.25                           | 2.07                           | 2.08                           | 2.08                           | 2.09                           | 2.11                           |
| dimethyl adipate          | 627-93-0| 1.83                           | 1.84                           | 1.85                           | 1.89                           | 1.96                           | 2.57                           | 2.57                           | 2.57                           | 2.53                           | 2.51                           |
| dimethyl phthalate        | 131-11-3| 0.92                           | 0.93                           | 0.93                           | 1.02                           | 1.16                           | 2.14                           | 2.14                           | 2.14                           | 2.18                           | 2.21                           |
| dimethyl succinate        | 106-65-0| 1.93                           | 1.94                           | 1.97                           | 2.03                           | 2.15                           | 3.06                           | 3.05                           | 3.04                           | 2.99                           | 2.86                           |
| dimethyl glutarate        | 1119-40-0| 1.97                          | 1.98                           | 1.99                           | 2.04                           | 2.13                           | 2.84                           | 2.83                           | 2.83                           | 2.80                           | 2.74                           |
| glycerol triacetate       | 102-76-1| 1.61                           | 1.62                           | 1.64                           | 1.69                           | 1.79                           | 2.49                           | 2.49                           | 2.49                           | 2.48                           | 2.43                           |
| triethyl citrate          | 77-93-0| 0.69                           | 0.70                           | 0.70                           | 0.72                           | 0.73                           | 1.40                           | 1.41                           | 1.41                           | 1.43                           | 1.45                           |
| ethyl lactate             | 97-64-3| 3.02                           | 3.01                           | 2.99                           | 2.94                           | 2.81                           | 3.24                           | 3.23                           | 3.21                           | 3.15                           | 3.02                           |
| 1,2-ethanediol diacetate  | 111-55-7| 2.65                           | 2.65                           | 2.64                           | 2.63                           | 2.58                           | 3.23                           | 3.21                           | 3.19                           | 3.10                           | 2.91                           |
| **Ketones**               |        |                               |                               |                               |                               |                               |                               |                               |                               |                               |                               |
|                  |          |       |       |       |       |       |       |       |
|------------------|----------|-------|-------|-------|-------|-------|-------|-------|
| methyl isobutyl ketone | 108-10-1 | 2.85  | 2.83  | 2.80  | 2.73  | 2.62  | 3.01  | 3.00  |
| cyclopentanone    | 120-92-3 | -     | -     | -     | -     | 2.41  | 2.38  | 2.33  |
| cyclohexanone     | 108-94-1 | 2.59  | 2.54  | 2.51  | 2.48  | 2.45  | 3.40  | 3.38  |
|                  |          |       |       |       |       |       |       |       |
| **Ethers**        |          |       |       |       |       |       |       |       |
| dimethoxymethane  | 109-87-5 | -     | -     | -     | -     | 3.40  | 3.37  | 3.32  |
| tetrahydrofuran   | 109-99-9 | -     | -     | -     | -     | 3.51  | 3.48  | 3.44  |
| 1,2-dimethoxyethane | 110-71-4 | -     | -     | -     | -     | 3.63  | 3.60  | 3.56  |
| 1,1,3-trimethoxypropane | 14315-97-0 | 2.67  | 2.66  | 2.64  | 2.58  | 2.47  | 2.52  | 2.52  |
| dipropylene glycol | 25265-71-8 | -     | -     | -     | -     | 3.82  | 2.80  | 2.72  |
| diglyme           | 111-96-6 | -     | -     | -     | -     | 3.34  | 3.33  | 3.30  |
| dimethyl isosorbide | 5306-85-4 | -     | -     | -     | -     | 2.76  | 2.75  | 2.73  |
| PEO              | 25322-68-3 | 2.43  | 2.42  | 2.40  | 2.33  | 2.21  | 2.60  | 2.60  |
|                  |          |       |       |       |       |       |       |       |
| **Organic carbonates** |          |       |       |       |       |       |       |       |
| dimethyl carbonate | 616-38-6 | 2.20  | 2.19  | 2.16  | 2.11  | 2.05  | 3.30  | 3.26  |
| diethyl carbonate | 105-58-8 | 2.01  | 2.00  | 1.97  | 1.92  | 1.85  | 2.93  | 2.92  |
| propylene carbonate | 108-32-7 | 1.86  | 1.84  | 1.79  | 1.73  | 1.65  | 2.55  | 2.51  |
| butylene carbonate | 4437-85-8 | 1.78  | 1.76  | 1.72  | 1.67  | 1.58  | 2.51  | 2.49  |
|                  |          |       |       |       |       |       |       |       |
| **Dipolar aprotic** |          |       |       |       |       |       |       |       |
| nitromethane      | 75-52-5  | 2.54  | 2.60  | 2.68  | 2.91  | 3.28  | -     | -     |
| n,n-dimethyloctanamide | 1118-92-9 | 2.34  | 2.33  | 2.31  | 2.25  | 2.12  | 2.07  | 2.05  |
| n,n-dimethyldecanamide | 14433-76-2 | 1.71  | 1.69  | 1.66  | 1.57  | 1.38  | 1.32  | 1.31  |
| hexamethylphosphoramid | 680-31-9 | -     | -     | -     | -     | 3.12  | 3.09  | 3.06  |
|                  |          |       |       |       |       |       |       |       |
| **Halogenated**   |          |       |       |       |       |       |       |       |
| dichloromethane   | 75-09-2  | 2.07  | 2.33  | 2.67  | 3.59  | 4.62  | 3.69  | 3.69  |
|                  |          |       |       |       |       |       |       |       |
| **Bases**         |          |       |       |       |       |       |       |       |
| pyridine          | 110-86-1 | -     | -     | 4.08  | 3.93  | 3.61  | 3.55  | 3.51  |
| tetramethylurea   | 632-22-4 | -     | -     | -     | -     | -     | -     | 3.03  |
| N,N'-Dimethylpropyleneurea | 7226-23-5 | -     | -     | -     | -     | 2.69  | 2.67  | 2.63  |
| 2,4,6-collidine   | 108-75-8 | 3.31  | 3.28  | 3.24  | 3.10  | 2.80  | 2.51  | 2.50  |
| methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate | 1174627-68-9 | 1.02  | -     | -     | -     | -     | 3.23  | 3.21  | 3.18  | 3.08  | 2.88  |
Table S4: Distribution coefficients calculated from COSMO-RS predictions of the LLE \((\text{H}_2\text{O} + 5\text{-HMF} + \text{solvent})\) at 298.15 K and 423.15 K for feed compositions simulated from different initial substrate concentrations. Note: the results for a feed composition corresponding to an initial concentration of xylose of 1% wt. at 423.15 K are marked in purple italic font for reference for the ranking of solvents. The results for MIBK are highlighted due this solvent being the most commonly applied in experimental studies. – denotes non-existing LLE.

| Solvent                        | CAS   | \(C_{\text{fwcd}}\) =1% wt. | \(C_{\text{fwcd}}\) =5% wt. | \(C_{\text{fwcd}}\) =10% wt. | \(C_{\text{fwcd}}\) =25% wt. | \(C_{\text{fwcd}}\) =50% wt. |
|-------------------------------|-------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| T=298.15 K                    |       |                               |                               |                               |                               |                               |
| Tetrahydrofurfuryl alcohol    | 97-99-4 | -                             | -                             | -                             | -                             | 1.92                          | 1.91                          | 1.90                          | -                             | 1.80                          |
| Furfuryl alcohol              | 98-00-0 | 8.37                          | 8.32                          | 8.27                          | 8.09                          | 7.79                          | 2.53                          | 2.53                          | 2.53                          | 2.53                          |
| 3-methoxy-3-methylbutanol     | 56539-66-3 | 2.68                          | 2.69                          | 2.70                          | 2.73                          | 2.81                          | 4.39                          | 4.38                          | 4.37                          | 4.33                          | 4.25                          |
| Benzyl alcohol                | 100-51-6 | 9.60                          | 9.55                          | 9.48                          | 9.27                          | 8.91                          | 5.76                          | 5.73                          | 5.69                          | 5.57                          | 5.32                          |
| Alcohol                       |       |                               |                               |                               |                               |                               |                               |                               |                               |                               |                               |
| Ethyl acetate                 | 6.64                           | 6.63                          | 6.63                          | 6.60                          | 6.56                          | 5.71                          | 5.69                          | 5.65                          | 5.55                          | 5.33                          |
| Isopropyl acetate             | 6.51                           | 6.52                          | 6.53                          | 6.58                          | 6.66                          | 5.52                          | 5.51                          | 5.50                          | 5.46                          | 5.37                          |
| n-Propyl acetate              | 6.61                           | 6.62                          | 6.63                          | 6.67                          | 6.75                          | 5.57                          | 5.56                          | 5.55                          | 5.51                          | 5.42                          |
| Adipic acid diethyl ester     | 4.09                           | 4.12                          | 4.15                          | 4.27                          | 4.50                          | 3.60                          | 3.61                          | 3.62                          | 3.65                          | 3.70                          |
| Acetic anhydride               | 8.02                           | 8.01                          | 8.00                          | 7.98                          | 7.90                          | 4.07                          | 4.05                          | 4.03                          | 3.96                          | 3.81                          |
| Methyl propionate             | 7.40                           | 7.39                          | 7.39                          | 7.37                          | 7.33                          | 5.85                          | 5.83                          | 5.80                          | 5.71                          | 5.50                          |
| Diethyl phthalate             | 3.74                           | 3.78                          | 3.83                          | 3.98                          | 4.30                          | 3.51                          | 3.52                          | 3.53                          | 3.57                          | 3.65                          |
| Ethyl succinate               | 4.63                           | 4.66                          | 4.70                          | 4.83                          | 5.08                          | 4.18                          | 4.18                          | 4.19                          | 4.20                          | 4.22                          |
| Diisobutyl succinate          | 2.61                           | 2.64                          | 2.67                          | 2.79                          | 3.06                          | 2.64                          | 2.65                          | 2.66                          | 2.71                          | 2.80                          |
| Dimethyl adipate              | 5.37                           | 5.39                          | 5.42                          | 5.50                          | 5.66                          | 4.49                          | 4.49                          | 4.49                          | 4.48                          | 4.44                          |
| Dimethyl phthalate            | 4.99                           | 5.02                          | 5.06                          | 5.18                          | 5.43                          | 4.33                          | 4.33                          | 4.33                          | 4.34                          | 4.33                          |
| Dimethyl succinate            | 6.12                           | 6.14                          | 6.16                          | 6.22                          | 6.33                          | 4.80                          | 4.79                          | 4.78                          | 4.72                          | 4.61                          |
| Benzoic acid phenylmethylster | 3.15                           | 3.19                          | 3.24                          | 3.42                          | 3.79                          | 3.19                          | 3.20                          | 3.22                          | 3.27                          | 3.37                          |
| Dimethyl glutarate            | 5.81                           | 5.83                          | 5.85                          | 5.92                          | 6.04                          | 4.76                          | 4.76                          | 4.75                          | 4.72                          | 4.64                          |
| Diisobutyl glutarate          | 2.45                           | 2.47                          | 2.50                          | 2.61                          | 2.85                          | 2.48                          | 2.48                          | 2.49                          | 2.53                          | 2.61                          |
| Glycerol triacetate           | 5.02                           | 5.05                          | 5.08                          | 5.18                          | 5.37                          | 4.15                          | 4.15                          | 4.15                          | 4.14                          | 4.11                          |
| Triethyl citrate              | 3.25                           | 3.29                          | 3.33                          | 3.48                          | 3.79                          | 3.05                          | 3.06                          | 3.08                          | 3.13                          | 3.23                          |
| Ethyl lactate                 | 5.55                           | 5.56                          | 5.58                          | 5.63                          | 5.72                          | 5.02                          | 5.01                          | 4.99                          | 4.94                          | 4.82                          |
| 1,2-ethanediol diacetate      | 5.93                           | 5.93                          | 5.94                          | 5.97                          | 6.01                          | 4.65                          | 4.63                          | 4.61                          | 4.55                          | 4.41                          |
| Ketones                       |       |                               |                               |                               |                               |                               |                               |                               |                               |                               |                               |
| Methyl isobutyl ketone        | 5.92                           | 5.93                          | 5.94                          | 5.98                          | 6.07                          | 5.36                          | 5.35                          | 5.34                          | 5.30                          | 5.22                          |
| Cyclopentanone                | 120-92-3                      | -                             | -                             | -                             | -                             | 2.74                          | 2.74                          | 2.73                          | 2.70                          | 2.65                          |
| Cyclohexanone                 | 108-94-1                      | 3.43                          | 3.41                          | 3.38                          | 3.33                          | 3.27                          | 4.51                          | 4.49                          | 4.47                          | 4.40                          | 4.25                          |
### Organic acids

| Acid                         | Molecular Weight | Boiling Point (°C) |
|------------------------------|------------------|-------------------|
| cis-9-octadecenoic acid      | 112-80-1         | 2.67              |
| ricinoleic acid              | 141-22-0         | 1.72              |

### Ethers

| Ethers                        | Molecular Weight | Boiling Point (°C) |
|-------------------------------|------------------|-------------------|
| dimethoxymethane              | 109-87-5         | -                 |
| tetrahydrofuran               | 109-99-9         | -                 |
| 1,2-dimethoxyethane           | 110-71-4         | -                 |
| 1,1,3-trimethoxypropane       | 14135-97-0       | 4.83              |
| dipropyleneeglycol            | 25265-71-8       | -                 |
| diglyme                       | 111-96-6         | 5.06              |
| anisole                       | 100-66-3         | 5.06              |
| dimethyl isosorbide           | 5306-85-4        | 3.84              |
| PEO                           | 25322-68-3       | 3.84              |

### Organic carbonates

| Carbonates                    | Molecular Weight | Boiling Point (°C) |
|-------------------------------|------------------|-------------------|
| dimethyl carbonate            | 616-38-6         | 5.32              |
| diethyl carbonate             | 105-58-8         | 4.91              |
| propylene carbonate           | 108-32-7         | 4.77              |
| butylene carbonate            | 4437-85-8        | 4.68              |

### Dipolar aprotic

| Aprotic                       | Molecular Weight | Boiling Point (°C) |
|-------------------------------|------------------|-------------------|
| nitromethane                  | 75-52-5          | 11.19             |
| n,n-dimethyloctanamide        | 1118-92-9        | 3.30              |
| hexamethylphosphoramide       | 680-31-9         | 2.08              |

### Halogenated

| Halogenated                   | Molecular Weight | Boiling Point (°C) |
|-------------------------------|------------------|-------------------|
| chloroform                    | 67-66-3          | 18.16             |
| dichloromethane               | 75-09-2          | 20.30             |
| cis-1,2-dichloroethene        | 156-59-2         | 10.77             |
| 1,2-dichloroethene            | 107-06-2         | 8.17              |

### Bases

| Bases                         | Molecular Weight | Boiling Point (°C) |
|-------------------------------|------------------|-------------------|
| pyridine                      | 110-86-1         | 5.05              |
| tetramethylurea               | 632-22-4         | -                 |
| N,N' Dimethylpropyleneurea    | 7226-23-5        | -                 |
| 2,4,6-collidine               | 108-75-8         | 4.83              |
| 1,2-dimethyl-3-nitrobenzene   | 83-41-0          | 3.71              |
| 1,3-dimethyl-2-nitrobenzene   | 81-20-9          | 3.36              |
| 1,4-dimethyl-2-nitrobenzene   | 89-58-7          | 3.50              |
| methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate | 1174627-68-9 | -                 |

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*Note: The values represent boiling points in °C.*