

Table S1. Data source for the VLE data sets studied (constant T) and summary of the results of the consistency tests and the inspection of the liquid Gibbs energy of mixing ( $g^{M,liq}$ ).

| no. | Components                      | T(°C) | Data source <sup>a</sup> | Area test | Point test | $g^{M,liq}$ b |
|-----|---------------------------------|-------|--------------------------|-----------|------------|---------------|
| 1   | water-nitromethane              | 50    | Vol. I, Part 1a, p 45    |           | -          | hd            |
| 2   | methanol-water                  | 25    | Vol. I, Part 1, p 42     | +         | +          | s             |
| 3   | methanol-water                  | 39,9  | Vol. I, Part 1b, p 32    | -         | -          | s             |
| 4   | methanol-water                  | 50    | Vol. I, Part 1c, p 77    | +         | +          | s             |
| 5   | acetonitrile-water              | 20    | Vol. I, Part 1b, p 37    | -         | -          | md            |
| 6   | ethylene oxide-water            | 10    | Vol. I, Part 1a, p 87    |           | +          | hd            |
| 7   | ethylene oxide-water            | 20    | Vol. I, Part 1a, p 88    |           | +          | hd            |
| 8   | ethanol-water                   | 25    | Vol. I, Part 1b, p 108   | +         | +          | s             |
| 9   | ethanol-water                   | 39,8  | Vol. I, Part 1, p 194    | +         | -          | md            |
| 10  | ethanol-water                   | 40    | Vol. I, Part 1, p 172    | +         | -          | md            |
| 11  | ethanol-water                   | 50    | Vol. I, Part 1, p 191    | -         | -          | md            |
| 12  | ethanol-water                   | 60    | Vol. I, Part 1, p 192    | -         | -          | md            |
| 13  | ethanol-water                   | 65    | Vol. I, Part 1a, p 147   | +         | -          | md            |
| 14  | ethanol-water                   | 70    | Vol. I, Part 1a, p 148   | +         | -          | md            |
| 15  | acetone-water                   | 25    | Vol. I, Part 1, p 245    | -         | -          | hd            |
| 16  | acetone-water                   | 30    | Vol. I, Part 1, p 246    | -         | -          | hd            |
| 17  | acetone-water                   | 30    | Vol. I, Part 1c, p 323   | -         | -          | md            |
| 18  | acetone-water                   | 35    | Vol. I, Part 1a, p 195   | +         | +          | md            |
| 19  | acetone-water                   | 35    | Vol. I, Part 1c, p 336   | +         | +          | md            |
| 20  | acetone-water                   | 45    | Vol. I, Part 1, p 247    | +         | +          | hd            |
| 21  | acetone-water                   | 50    | Vol. I, Part 1c, p 337   | +         | +          | md            |
| 22  | acetone-water                   | 20    | Vol. I, Part 1c, p 335   | +         | +          | md            |
| 23  | water-acetone                   | 60    | Vol. I, Part 1, p 248    | +         | +          | md            |
| 24  | acetone-water                   | 100   | Vol. I, Part 1a, p 194   | +         | +          | md            |
| 25  | allyl alcohol-water             | 40    | Vol. I, Part 1, p 252    | -         | -          | s             |
| 26  | 1,3-dioxolane-water             | 70    | Vol. I, Part 1a, p 212   | +         | -          | hd            |
| 27  | water-n,n-dimethyl-formamide    | 60    | Vol. I, Part 1c, p 399   | -         | +          | s             |
| 28  | 1-propanol-water                | 25    | Vol. I, Part 1, p 285    | -         | -          | md            |
| 29  | 1-propanol-water                | 40    | Vol. I, Part 1, p 293    | -         | -          | md            |
| 30  | 2-propanol-water                | 45    | Vol. I, Part 1, p 326    | -         | -          | md            |
| 31  | 2-propanol-water                | 60    | Vol. I, Part 1, p 327    | -         | -          | md            |
| 32  | 2-propanol-water                | 65    | Vol. I, Part 1, p 323    | +         | +          | md            |
| 33  | 2-propanol-water                | 150   | Vol. I, Part 1b, p 169   | +         | +          | md            |
| 34  | water-1,4-dioxane               | 25    | Vol. I, Part 1, p 390    | +         | -          | s             |
| 35  | water-1,4-dioxane               | 35    | Vol. I, Part 1, p 386    | +         | -          | md            |
| 36  | pirrolidina-water               | 80    | Vol. I, Part 1c, p 565   | +         | +          | s             |
| 37  | terc-butanol-water              | 25    | Vol. I, Part 1, p 423    | +         | -          | md            |
| 38  | terc-butanol-water              | 75    | Vol. I, Part 1, p 425    | -         | -          | md            |
| 39  | diethylamine-water              | 56,8  | Vol. I, Part 1, p 453    | +         | +          | s             |
| 40  | pyridine-water                  | 80    | Vol. I, Part 1, p 475    | -         | -          | md            |
| 41  | pyridine-water                  | 93,2  | Vol. I, Part 1a, p 370   | -         | -          | md            |
| 42  | water-pyridine                  | 27    | Vol. I, Part 1a, p 366   | +         | -          | md            |
| 43  | water-pyridine                  | 30    | Vol. I, Part 1, p 465    | -         | -          | s             |
| 44  | water-4-methylpyridine          | 69,9  | Vol. I, Part 1, p 507    | +         | +          | s             |
| 45  | diacetone alcohol-water         | 66,8  | Vol. I, Part 1d, p 108   | -         | -          | hd            |
| 46  | triethylamine-water             | 10    | Vol. I, Part 1b, p 346   | +         | -          | hd            |
| 47  | triethylamine-water             | 18    | Vol. I, Part 1b, p 347   | +         | -          | hd            |
| 48  | acrylonitrile-water             | 40    | Vol. I, Part 1, p 221    | -         | +          | hd            |
| 49  | acetic acid, methyl ester-water | 35    | Vol. I, Part 1, p 259    | -         | +          | hd            |

|    |                                 |       |                         |   |   |    |
|----|---------------------------------|-------|-------------------------|---|---|----|
| 50 | acetic acid, methyl ester-water | 50    | Vol. I, Part 1, p 260   | + | - | hd |
| 51 | 2-butanone-water                | 60    | Vol. I, Part 1A, p 271  | + | - | hd |
| 52 | 2-butanol-water                 | 40    | Vol. I, Part 1b, p 256  | - | - | s  |
| 53 | 2-butanol-water                 | 60    | Vol. I, Part 1, p 414   | + | - | hd |
| 54 | 1-butanol-water                 | 60    | Vol. I, Part 1, p 411   | + | - | hd |
| 55 | 2-butanol-water                 | 80    | Vol. I, Part 1, p 415   | - | - | hd |
| 56 | furfural-water                  | 80    | Vol. I, Part 1a, p 360  | - | - | hd |
| 57 | water-aniline                   | 100   | Vol. I, Part 1, p 497   |   | - | hd |
| 58 | water-3-methylpyridine          | 130,2 | Vol. I, Part 1, p 505   | + | + | s  |
| 59 | water-cyclohexanol              | 90    | Vol. I, Part 1, p 514   | - | - | hd |
| 60 | water-1-hexanol                 | 40    | Vol. I, Part 1b, p 343  | - | + | hd |
| 61 | water-2-butoxy-ethanol          | 110   | Vol. I, Part 1, p 527   | + | + | s  |
| 62 | o-deuteromethanol-water         | 25    | Vol. I, Part 1b, p. 20  | + | + | s  |
| 63 | 2,2,2 trifluoethanol-water      | 25    | Vol. I, Part 1c, p 114  | + | + | hd |
| 64 | 2,2,2 trifluoethanol-water      | 106,2 | Vol. I, Part 1c, p 118  | - | - | hd |
| 65 | 2,2,2 trifluoethanol-water      | 126   | Vol. I, Part 1c, p. 119 | - | - | hd |
| 66 | o-deuteroethanol-water          | 25    | Vol. I, Part 1b, p 82   | + | + | s  |
| 67 | acetic acid anhydride           | 80    | Vol. I, Part 1b, p 198  | - | - | hd |
| 68 | water-morfoline                 | 75,2  | Vol. I, Part 1c, p 568  | - | + | s  |
| 69 | water-1-metoxo-2-propanol       | 80    | Vol. I, Part 1d, p 16   | + | + | s  |
| 70 | water-2-etoxoethanol            | 90    | Vol. I, Part 1d, p 13   | + | + | s  |
| 71 | water-2-isopropoxietanol        | 95    | Vol. I, Part 1d, p 110  | - | - | hd |
| 72 | methyl-diethylamine-water       | 35    | Vol. I, Part 1, p 490   | + | + | s  |

(<sup>a</sup>) J.M. Sørensen, W. Artl, Vapor-Liquid Equilibrium Data Collection; Aqueous-Organics Systems. Chemistry Data Series, DECHEMA, Frankfurt.

(<sup>b</sup>) s: smooth, md: moderate dispersion, hd: high dispersion

Table S2. Data source for the VLE data sets studied (constant P) and summary of the results of the consistency tests and the inspection of the liquid Gibbs energy of mixing ( $g^{M,liq}$ ).

| no. | System components          | P<br>(mmHg) | Data source <sup>a</sup> | Area<br>test | Point<br>test | $g^{M,liq}$ <sup>b</sup> |
|-----|----------------------------|-------------|--------------------------|--------------|---------------|--------------------------|
| 73  | methanol-water             | 760         | Vol. I, Part 1a, p 58    | +            | +             | s                        |
| 74  | acetonitrile-water         | 760         | Vol. I, Part 1, p 80     | +            | -             | hd                       |
| 75  | water-2-chloroethanol      | 100         | Vol. I, Part 1, p 143    | +            | -             | hd                       |
| 76  | water-2-chloroethanol      | 200         | Vol. I, Part 1, p 140    | -            | -             | md                       |
| 77  | water-n-methylformamide    | 760         | Vol. I, Part 1, p 148    | +            | -             | md                       |
| 78  | acetone-water              | 760         | Vol. I, Part 1, p 236    | -            | +             | s                        |
| 79  | water-1,2-propanediol      | 25          | Vol. I, Part 1, p 336    | -            | -             | hd                       |
| 80  | water-1,2-propanediol      | 50          | Vol. I, Part 1, p 337    | -            | +             | hd                       |
| 81  | 1-propanol-water           | 758         | Vol. I, Part 1, p 287    | +            | -             | hd                       |
| 82  | isopropylamine-water       | 760         | Vol. I, Part 1b, p 189   | -            | -             | hd                       |
| 83  | metilvinilcetona-water     | 743         | Vol. I, Part 1, p 355    | +            | -             | hd                       |
| 84  | tetrahydrofurane-water     | 760         | Vol. I, Part 1, p 370    | -            | -             | hd                       |
| 85  | water-3-hydroxy-2-butanone | 750         | Vol. I, Part 1, p 399    | +            | +             | hd                       |
| 86  | water-2,3-butanediol       | 200         | Vol. I, Part 1, p 443    | -            | -             | hd                       |
| 87  | water-2,3-butanediol       | 350         | Vol. I, Part 1, p 444    | -            | +             | hd                       |
| 88  | water-2,3-butanediol       | 750         | Vol. I, Part 1, p 442    | -            | +             | hd                       |
| 89  | water-2,3-butanediol       | 760         | Vol. I, Part 1, p 446    | -            | -             | hd                       |

(<sup>a</sup>) Sørensen J.M., and Artl W., Vapor-Liquid Equilibrium Data Collection; Aqueous-Organics Systems. Chemistry Data Series, DECHEMA, Frankfurt.

(<sup>b</sup>) s: smooth, md: moderate dispersion, hd: high dispersion