

**Table S1. Experimental LLE Data on Mole Fraction, Solute Distribution Ratio,  $\beta$ , and Selectivity,  $S$ , for the Studied Ternary Systems at  $T = 298.15$  K and Atmospheric Pressure.**

| Upper phase                                       |         | Lower phase |            | $\beta$ | $S$   |
|---------------------------------------------------|---------|-------------|------------|---------|-------|
| $x_1^I$                                           | $x_2^I$ | $x_1^{II}$  | $x_2^{II}$ |         |       |
| {Heptane (1) + Toluene (2) + [EMim][OAc] (3)}     |         |             |            |         |       |
| 1.000                                             | 0.000   | 0.011       | 0.000      | -       | -     |
| 0.962                                             | 0.038   | 0.006       | 0.011      | 0.29    | 46.41 |
| 0.882                                             | 0.118   | 0.006       | 0.027      | 0.23    | 33.64 |
| 0.809                                             | 0.191   | 0.006       | 0.039      | 0.20    | 27.53 |
| 0.712                                             | 0.288   | 0.005       | 0.056      | 0.19    | 27.69 |
| 0.608                                             | 0.392   | 0.005       | 0.066      | 0.17    | 20.47 |
| 0.503                                             | 0.497   | 0.005       | 0.087      | 0.18    | 17.61 |
| 0.412                                             | 0.588   | 0.005       | 0.095      | 0.16    | 13.31 |
| 0.291                                             | 0.709   | 0.004       | 0.110      | 0.16    | 11.29 |
| 0.206                                             | 0.794   | 0.003       | 0.134      | 0.17    | 11.59 |
| 0.000                                             | 1.000   | 0.000       | 0.213      | 0.21    | -     |
| {Cyclohexane (1) + Toluene (2) + [EMim][OAc] (3)} |         |             |            |         |       |
| 1.000                                             | 0.000   | 0.021       | 0.000      | -       | -     |
| 0.900                                             | 0.100   | 0.011       | 0.015      | 0.15    | 12.27 |
| 0.797                                             | 0.203   | 0.012       | 0.028      | 0.14    | 9.16  |
| 0.704                                             | 0.296   | 0.012       | 0.041      | 0.14    | 8.13  |
| 0.619                                             | 0.381   | 0.012       | 0.054      | 0.14    | 7.31  |
| 0.547                                             | 0.453   | 0.012       | 0.064      | 0.14    | 6.44  |
| 0.438                                             | 0.562   | 0.012       | 0.077      | 0.14    | 5.00  |
| 0.348                                             | 0.652   | 0.011       | 0.093      | 0.14    | 4.51  |
| 0.226                                             | 0.774   | 0.010       | 0.108      | 0.14    | 3.15  |
| 0.140                                             | 0.860   | 0.007       | 0.134      | 0.16    | 3.12  |
| 0.000                                             | 1.000   | 0.000       | 0.213      | 0.21    | -     |
| {Heptane (1) + Cyclohexane (2) + [EMim][OAc] (3)} |         |             |            |         |       |
| 1.000                                             | 0.000   | 0.011       | 0.000      | -       | -     |
| 0.984                                             | 0.016   | 0.011       | 0.001      | 0.06    | 5.59  |
| 0.903                                             | 0.097   | 0.005       | 0.002      | 0.02    | 3.72  |
| 0.782                                             | 0.218   | 0.006       | 0.006      | 0.03    | 3.59  |
| 0.662                                             | 0.338   | 0.004       | 0.008      | 0.02    | 3.92  |

|       |       |       |       |      |      |
|-------|-------|-------|-------|------|------|
| 0.565 | 0.435 | 0.004 | 0.011 | 0.03 | 3.57 |
| 0.403 | 0.597 | 0.002 | 0.013 | 0.02 | 4.39 |
| 0.257 | 0.743 | 0.001 | 0.015 | 0.02 | 5.19 |
| 0.000 | 1.000 | 0.000 | 0.021 | 0.02 | -    |

Standard uncertainties  $u$  are  $u(x) = \pm 0.004$  and  $u(T) = \pm 0.01$  K.

**Table S2. Experimental and Calculated LLE Data with the NRTL Model, Solute Distribution Ratio,  $\beta$ , and Selectivity,  $S_{1+2}$ , for the Quaternary System {Heptane (1) + Cyclohexane (2) + Toluene (3) + [EMim][OAc] (4)} at  $T = 298.15$  K and Atmospheric Pressure.**

| Upper Phase |         |         | Lower Phase |            |            |            |            |            |         |           |
|-------------|---------|---------|-------------|------------|------------|------------|------------|------------|---------|-----------|
| Exp.        |         |         | Exp.        |            |            | NRTL       |            |            | $\beta$ | $S_{1+2}$ |
| $x_1^I$     | $x_2^I$ | $x_3^I$ | $x_1^{II}$  | $x_2^{II}$ | $x_3^{II}$ | $x_1^{II}$ | $x_2^{II}$ | $x_3^{II}$ |         |           |
| 0.715       | 0.120   | 0.165   | 0.005       | 0.003      | 0.042      | 0.005      | 0.004      | 0.037      | 0.25    | 26.57     |
| 0.674       | 0.144   | 0.182   | 0.004       | 0.004      | 0.046      | 0.004      | 0.004      | 0.040      | 0.25    | 25.84     |
| 0.522       | 0.111   | 0.367   | 0.004       | 0.004      | 0.088      | 0.004      | 0.004      | 0.079      | 0.24    | 18.97     |
| 0.430       | 0.132   | 0.438   | 0.003       | 0.004      | 0.100      | 0.003      | 0.004      | 0.093      | 0.23    | 18.33     |
| 0.340       | 0.120   | 0.540   | 0.003       | 0.004      | 0.101      | 0.002      | 0.004      | 0.110      | 0.19    | 12.29     |
| 0.232       | 0.119   | 0.649   | 0.002       | 0.005      | 0.130      | 0.002      | 0.005      | 0.128      | 0.20    | 10.04     |
| 0.103       | 0.118   | 0.779   | 0.001       | 0.005      | 0.147      | 0.001      | 0.006      | 0.147      | 0.19    | 6.95      |
| 0.638       | 0.258   | 0.104   | 0.005       | 0.008      | 0.026      | 0.005      | 0.007      | 0.024      | 0.25    | 17.23     |
| 0.595       | 0.230   | 0.175   | 0.004       | 0.007      | 0.040      | 0.004      | 0.006      | 0.040      | 0.23    | 17.14     |
| 0.496       | 0.243   | 0.261   | 0.003       | 0.008      | 0.062      | 0.003      | 0.007      | 0.059      | 0.24    | 15.96     |
| 0.424       | 0.191   | 0.385   | 0.003       | 0.006      | 0.087      | 0.003      | 0.006      | 0.084      | 0.23    | 15.44     |
| 0.312       | 0.221   | 0.467   | 0.002       | 0.008      | 0.098      | 0.002      | 0.008      | 0.101      | 0.21    | 11.19     |
| 0.231       | 0.257   | 0.512   | 0.002       | 0.010      | 0.116      | 0.002      | 0.010      | 0.110      | 0.23    | 9.21      |
| 0.116       | 0.233   | 0.651   | 0.001       | 0.010      | 0.131      | 0.001      | 0.010      | 0.132      | 0.20    | 6.38      |
| 0.553       | 0.350   | 0.097   | 0.004       | 0.011      | 0.026      | 0.004      | 0.010      | 0.023      | 0.27    | 16.14     |
| 0.497       | 0.334   | 0.169   | 0.004       | 0.011      | 0.040      | 0.003      | 0.010      | 0.040      | 0.24    | 13.11     |
| 0.396       | 0.346   | 0.258   | 0.003       | 0.012      | 0.061      | 0.003      | 0.011      | 0.060      | 0.24    | 11.70     |

|       |       |       |       |       |       |       |       |       |      |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|-------|
| 0.322 | 0.277 | 0.401 | 0.003 | 0.010 | 0.091 | 0.002 | 0.009 | 0.090 | 0.23 | 10.46 |
| 0.215 | 0.320 | 0.465 | 0.002 | 0.013 | 0.100 | 0.002 | 0.012 | 0.103 | 0.22 | 7.67  |
| 0.115 | 0.348 | 0.537 | 0.001 | 0.013 | 0.109 | 0.001 | 0.014 | 0.116 | 0.20 | 6.71  |
| 0.438 | 0.457 | 0.105 | 0.003 | 0.014 | 0.026 | 0.003 | 0.014 | 0.026 | 0.25 | 13.04 |
| 0.403 | 0.433 | 0.164 | 0.002 | 0.013 | 0.04  | 0.003 | 0.013 | 0.039 | 0.24 | 13.59 |
| 0.298 | 0.436 | 0.266 | 0.002 | 0.015 | 0.064 | 0.002 | 0.014 | 0.063 | 0.24 | 10.39 |
| 0.220 | 0.361 | 0.419 | 0.001 | 0.013 | 0.092 | 0.002 | 0.013 | 0.094 | 0.22 | 9.11  |
| 0.108 | 0.426 | 0.466 | 0.000 | 0.015 | 0.095 | 0.001 | 0.016 | 0.103 | 0.20 | 7.60  |
| 0.363 | 0.541 | 0.096 | 0.002 | 0.017 | 0.026 | 0.002 | 0.017 | 0.024 | 0.27 | 12.89 |
| 0.304 | 0.533 | 0.163 | 0.002 | 0.016 | 0.04  | 0.002 | 0.017 | 0.040 | 0.25 | 11.41 |
| 0.199 | 0.540 | 0.261 | 0.001 | 0.019 | 0.065 | 0.001 | 0.019 | 0.062 | 0.25 | 9.20  |
| 0.120 | 0.456 | 0.424 | 0.000 | 0.016 | 0.092 | 0.001 | 0.017 | 0.096 | 0.22 | 7.81  |
| 0.260 | 0.641 | 0.099 | 0.001 | 0.020 | 0.026 | 0.002 | 0.022 | 0.024 | 0.26 | 11.27 |
| 0.202 | 0.630 | 0.168 | 0.001 | 0.019 | 0.039 | 0.001 | 0.022 | 0.040 | 0.23 | 9.66  |
| 0.101 | 0.623 | 0.276 | 0.000 | 0.024 | 0.071 | 0.001 | 0.024 | 0.065 | 0.26 | 7.76  |
| 0.183 | 0.720 | 0.097 | 0.001 | 0.023 | 0.026 | 0.001 | 0.026 | 0.023 | 0.27 | 10.09 |
| 0.099 | 0.736 | 0.165 | 0.000 | 0.022 | 0.039 | 0.001 | 0.027 | 0.039 | 0.24 | 8.97  |
| 0.092 | 0.811 | 0.097 | 0.000 | 0.026 | 0.027 | 0.000 | 0.030 | 0.022 | 0.28 | 9.67  |

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Standard uncertainties  $u$  are  $u(x) = \pm 0.004$  and  $u(T) = \pm 0.01$  K