Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Electronic Supplementary Information**

# A Quantitative Thermodynamic Metric for Identifying Deep Eutectic Solvents

Bricker Like, Christina E. Uhlenbrock, and Matthew J. Panzer*

Department of Chemical & Biological Engineering, Tufts University

4 Colby Street, Medford, MA 02155 USA

*Email: matthew.panzer@tufts.edu

## I. Supplementary Discussion Regarding Higher Order Mixtures

Equations 1-3 presented in the main text (and reproduced here) conceptually define the dimensionless thermodynamic non-ideality metric $g^E$ and express its value at the eutectic point in terms of the eutectic composition (with species mole fractions $x_{i,e}$), temperature ($T_e$), and approximated species activity coefficients ($\gamma_{i,e}$), the latter being obtained from a simplified solid-liquid mixture phase equilibrium criterion:

$$(1)\quad g^E = \Delta g_{mix} - \Delta g_{mix}^{ideal}$$

$$(2)\quad \frac{g^E}{RT_e} = \sum_i x_{i,e}\, ln\, \gamma_{i,e}$$

$$(3)\quad ln\, \gamma_{i,e} = \frac{\Delta h_{fus,i}}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T_e}\right) - ln\, x_{i,e}$$

recalling that $R$ is the universal gas constant, $\Delta h_{fus,i}$ is the enthalpy of fusion of pure species 'i', and $T_{m,i}$ is the melting temperature of pure species 'i'. Importantly, these equations are valid for mixtures containing any number of components $n$, not only binary mixtures ($n$ = 2).

To illustrate how $g^E/RT_e$ can be determined for higher order mixtures, two ternary "DES" mixtures that had been experimentally studied by Abranches et al.[1] were considered: betaine:urea:water, and ChCl:urea:water. The pure component properties for betaine, ChCl, and urea are shown in Table S1; for water, $T_{m,i}$ = 273 K and $\Delta h_{fus,i}$ = 6.0 kJ/mol. According to the findings of Abranches et al.,[1] the eutectic composition for the ternary betaine:urea:water is located at $x_{betaine}$ = 0.364, $x_{urea}$ = 0.550, and $x_{water}$ = 0.086, with $T_e$ = 244.5 K. Substitution of the relevant parameters and these values into Equations 2 and 3 yields a $g^E/RT_e$ value of –2.52 for this mixture. Similarly, the eutectic point presented for the ternary ChCl:urea:water mixture ($x_{ChCl}$ = 0.273, $x_{urea}$ = 0.640, and $x_{water}$ = 0.087; $T_e$ = 295.4 K) yields a $g^E/RT_e$ value of –0.413. Both of these ternary systems meet the threshold for identifying a true DES presented in this work ($g^E/RT_e \leq$ –1/3).

## II. Supplementary Tables and Figures

**Table S1.** Summary of relevant thermodynamic parameters, reported eutectic point data, and literature references for each system analyzed in this work.

| HBA | HBD | $T_{m,HBA}$ [K] | $\Delta h_{fus,HBA}$ [kJ/mol] | $T_{m,HBD}$ [K] | $\Delta h_{fus,HBD}$ [kJ/mol] | $x_e$ (HBA) | $T_e$ [K] | Ref. # |
|---|---|---|---|---|---|---|---|---|
| betaine | camphor | 566 | 17.98 | 450.4 | 5.28 | 0.3 | 383.8 | [2] |
| betaine | coumarin | 566 | 17.98 | 342.3 | 18.63 | 0.4 | 334.4 | [2] |
| betaine | salicylic acid | 566 | 17.98 | 432.5 | 23.05 | 0.3 | 383.6 | [2] |
| betaine | thymol | 566 | 17.98 | 323.5 | 19.65 | 0.25 | 258 | [2] |
| betaine | urea | 566 | 17.98 | 406.7 | 14.6 | 0.2 | 359.1 | [2] |
| ChCl | 2,3-xylenol | 597 | 4.3 | 346.0 | 21.02 | 0.25 | 290.7 | [3] |
| ChCl | caffeic acid | 597 | 4.3 | 505.7 | 27.68 | 0.6667 | 340 | [4] |
| ChCl | camphor | 597 | 4.3 | 450.4 | 5.28 | 0.5 | 328.5 | [2] |
| ChCl | citric acid | 597 | 4.3 | 427.2 | 25.03 | 0.5 | 342 | [5] |
| ChCl | coumarin | 597 | 4.3 | 342.3 | 18.63 | 0.5 | 338.3 | [2] |
| ChCl | D-fructose | 597 | 4.3 | 466.4 | 22.77 | 0.667 | 283 | [6] |
| ChCl | D-glucose | 597 | 4.3 | 414.0 | 31.42 | 0.667 | 288 | [7] |
| ChCl | ethylene glycol | 597 | 4.3 | 260.6 | 9.9 | 0.1709 | 244 | [8] |
| ChCl | gallic acid | 597 | 4.3 | 641.0 | 30.96 | 0.667 | 350 | [4] |
| ChCl | glycerol | 597 | 4.3 | 293.0 | 18.28 | 0.333 | 237 | [9] |
| ChCl | imidazole | 597 | 4.3 | 361.9 | 12.82 | 0.3 | 329 | [10] |
| ChCl | L-(+)-tartaric acid | 597 | 4.3 | 448.0 | 18.62 | 0.667 | 320 | [4] |
| ChCl | L-menthol | 597 | 4.3 | 315.7 | 12.89 | 0.5 | 334.9 | [2] |
| ChCl | malonic acid | 597 | 4.3 | 407.5 | 23.1 | 0.5 | 283 | [5] |
| ChCl | o-cresol | 597 | 4.3 | 305.4 | 14.8 | 0.25 | 249 | [3] |
| ChCl | oxalic acid | 597 | 4.3 | 464.5 | 12.31 | 0.5 | 307 | [5] |
| ChCl | p-coumaric acid | 597 | 4.3 | 492.4 | 27.42 | 0.667 | 340 | [4] |
| ChCl | phenylacetic acid | 597 | 4.3 | 349.9 | 14.49 | 0.333 | 298 | [5] |
| ChCl | phenylpropionic acid | 597 | 4.3 | 321.2 | 15.61 | 0.333 | 293 | [5] |
| ChCl | salicylic acid | 597 | 4.3 | 432.5 | 23.05 | 0.5 | 340.4 | [5] |
| ChCl | succinic acid | 597 | 4.3 | 455.2 | 34.0 | 0.5 | 344 | [5] |
| ChCl | trans-cinnamic acid | 597 | 4.3 | 406.1 | 22.21 | 0.5 | 366 | [4] |
| ChCl | urea | 597 | 4.3 | 406.7 | 14.6 | 0.333 | 296.5 | [11] |
| TBAB | imidazole | 395 | 15.48 | 361.9 | 12.82 | 0.3 | 294 | [10] |
| TBAC | ethylene glycol | 344 | 14.69 | 260.6 | 9.9 | 0.25 | 242.1 | [12] |
| TBAC | glycerol | 344 | 14.69 | 293.0 | 18.28 | 0.1667 | 229.2 | [12] |
| TBAC | triethylene glycol | 344 | 14.69 | 263.8 | 21.85 | 0.75 | 260.3 | [12] |

**Table S2.** Summary of calculated thermodynamic metrics, activity coefficients, and ideal eutectic point data for each system analyzed in this work.

| HBA | HBD | $g^E/RT_e$ | $\gamma_{HBA}$ | $\gamma_{HBD}$ | $x_e^{ideal}$ (HBA) | $T_e^{ideal}$ [K] | $D_e$ | $\lvert x_e - x_e^{ideal} \rvert$ |
|---|---|---|---|---|---|---|---|---|
| betaine | camphor | -0.105 | 0.543 | 1.119 | 0.186 | 393 | -2.3 | 0.11 |
| betaine | coumarin | -0.478 | 0.177 | 1.428 | 0.076 | 338.2 | -1.1 | 0.32 |
| betaine | salicylic acid | -0.506 | 0.542 | 0.631 | 0.247 | 414.2 | -7.4 | 0.05 |
| betaine | thymol | -1.969 | 0.042 | 0.209 | 0.054 | 321.1 | -19.7 | 0.20 |
| betaine | urea | -0.398 | 0.553 | 0.705 | 0.176 | 389.2 | -7.7 | 0.02 |
| ChCl | 2,3-xylenol | -0.708 | 1.606 | 0.332 | 0.469 | 318.4 | -8.7 | 0.22 |
| ChCl | caffeic acid | -0.869 | 0.779 | 0.121 | 0.707 | 426.3 | -20.2 | 0.04 |
| ChCl | camphor | 0.077 | 0.985 | 1.185 | 0.458 | 314 | 4.6 | 0.04 |
| ChCl | citric acid | -0.507 | 1.048 | 0.346 | 0.604 | 377.5 | -9.4 | 0.10 |
| ChCl | coumarin | 0.323 | 1.031 | 1.851 | 0.456 | 313.2 | 8.0 | 0.04 |
| ChCl | D-fructose | -1.272 | 0.573 | 0.067 | 0.645 | 396.5 | -28.6 | 0.02 |
| ChCl | D-glucose | -1.314 | 0.592 | 0.055 | 0.601 | 376.1 | -23.4 | 0.07 |
| ChCl | ethylene glycol | -0.015 | 1.671 | 0.884 | 0.283 | 242.9 | 0.5 | 0.11 |
| ChCl | gallic acid | -1.380 | 0.813 | 0.024 | 0.83 | 491.3 | -28.8 | 0.16 |
| ChCl | glycerol | -0.985 | 0.805 | 0.255 | 0.366 | 276.2 | -14.2 | 0.03 |
| ChCl | imidazole | 0.101 | 1.646 | 0.933 | 0.463 | 315.9 | 4.1 | 0.16 |
| ChCl | L-(+)-tartaric acid | -0.530 | 0.708 | 0.407 | 0.605 | 377.8 | -15.3 | 0.06 |
| ChCl | L-menthol | 0.495 | 1.015 | 2.650 | 0.392 | 286.7 | 16.8 | 0.11 |
| ChCl | malonic acid | -1.287 | 0.765 | 0.100 | 0.571 | 362.5 | -21.9 | 0.07 |
| ChCl | o-cresol | -0.731 | 1.192 | 0.356 | 0.381 | 282.2 | -11.8 | 0.13 |
| ChCl | oxalic acid | -0.534 | 0.882 | 0.390 | 0.578 | 365.6 | -16.0 | 0.08 |
| ChCl | p-coumaric acid | -0.800 | 0.779 | 0.149 | 0.692 | 418.8 | -18.8 | 0.02 |
| ChCl | phenylacetic acid | -0.232 | 1.259 | 0.630 | 0.453 | 312.1 | -4.5 | 0.12 |
| ChCl | phenylpropionic acid | -0.038 | 1.222 | 0.854 | 0.411 | 294.5 | -0.5 | 0.08 |
| ChCl | salicylic acid | -0.501 | 1.041 | 0.353 | 0.605 | 377.8 | -9.9 | 0.11 |
| ChCl | succinic acid | -1.077 | 1.058 | 0.110 | 0.665 | 405.8 | -15.2 | 0.17 |
| ChCl | trans-cinnamic acid | 0.059 | 1.158 | 0.973 | 0.566 | 360.4 | 1.6 | 0.07 |
| ChCl | urea | -0.727 | 1.248 | 0.301 | 0.533 | 345.8 | -14.3 | 0.20 |
| TBAB | imidazole | -0.564 | 0.660 | 0.534 | 0.371 | 326.4 | -9.9 | 0.07 |
| TBAC | ethylene glycol | -0.240 | 0.460 | 0.940 | 0.152 | 251.6 | -3.8 | 0.10 |
| TBAC | glycerol | -1.719 | 0.458 | 0.149 | 0.305 | 279.4 | -18.0 | 0.14 |
| TBAC | triethylene glycol | -0.709 | 0.256 | 3.505 | 0.183 | 258.5 | 0.7 | 0.57 |

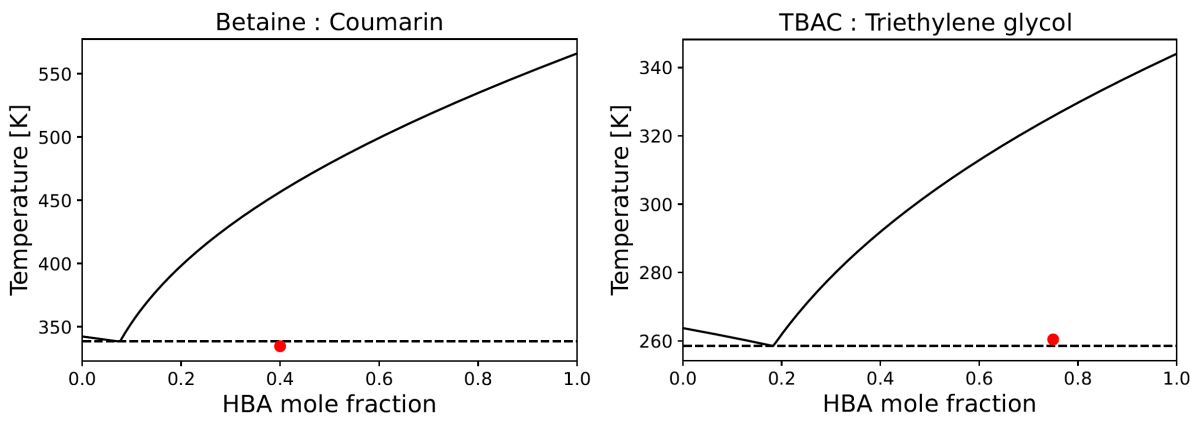


**Figure S1.** Schematic ideal solid-liquid phase diagrams of temperature versus composition (isobaric, at 1 bar) for two binary mixtures: (a) betaine:coumarin, (b) TBAC:triethylene glycol. Solid black curves indicate the liquidus boundary of the hypothetical ideal mixture, which converge at the ideal eutectic temperature (horizontal dashed black line). Solid red marker indicates the location of the experimentally measured eutectic point, according to literature reports.[2, 12] Both mixtures exhibit a substantial shift in their eutectic composition versus that of the ideal cases, in addition to very small $\Delta T$ values.

## Supplementary Notes and References


1. D. O. Abranches, L. P. Silva, M. A. R. Martins and J. A. P. Coutinho, *J. Chem. Phys.*, 2021, **155**, 034501.
2. D. O. Abranches, L. P. Silva, M. A. R. Martins, S. P. Pinho and J. A. P. Coutinho, *ChemSusChem*, 2020, **13**, 4916-4921.
3. W. J. Guo, Y. C. Hou, S. H. Ren, S. D. Tian and W. Z. Wu, *J Chem Eng Data*, 2013, **58**, 866-872.
4. Z. Maugeri and P. Domínguez de María, *RSC Adv.*, 2012, **2**, 421-425.
5. A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *J. Am. Chem. Soc.*, 2004, **126**, 9142-9147.
6. A. Hayyan, F. S. Mjalli, I. M. AlNashef, T. Al-Wahaibi, Y. M. Al-Wahaibi and M. A. Hashim, *Thermochim. Acta*, 2012, **541**, 70-75.
7. A. Hayyan, F. S. Mjalli, I. M. AlNashef, Y. M. Al-Wahaibi, T. Al-Wahaibi and M. A. Hashim, *J. Mol. Liq.*, 2013, **178**, 137-141.

8. V. Agieienko and R. Buchner, *Phys. Chem. Chem. Phys.*, 2022, **24**, 5265-5268.
9. K. Shahbaz, S. Baroutian, F. S. Mjalli, M. A. Hashim and I. M. AlNashef, *Thermochim. Acta*, 2012, **527**, 59-66.
10. Y. W. Hou, Y. Y. Gu, S. M. Zhang, F. Yang, H. M. Ding and Y. K. Shan, *J. Mol. Liq.*, 2008, **143**, 154-159.
11. X. Meng, K. Ballerat-Busserolles, P. Husson and J.-M. Andanson, *New J. Chem.*, 2016, **40**, 4492-4499.
12. F. S. Mjalli, J. Naser, B. Jibril, V. Alizadeh and Z. Gano, *J. Chem. Eng. Data*, 2014, **59**, 2242-2251.