

Comment on “Structural Study of a Eutectic Solvent Reveals Hydrophobic Segregation and Lack of Hydrogen Bonding between the Components”

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The emergence of sustainable chemistry drives the search for greener solvents capable of substituting or improving upon petroleum-derived and toxic ones. In this context, deep eutectic solvents (DES) emerged as promising alternatives for a wide variety of applications due to their simple preparation and versatility, which can be modulated by varying the selection and ratio of the hydrogen bond donor and acceptor.¹ Nevertheless, a number of misconceptions persist in the literature including the following: (i) the presence of a eutectic solvent in a binary mixture is in itself remarkable, (ii) a melting point decrease in eutectic systems below that of the pure compounds, or (iii) the existence of hydrogen bonding interactions in the mixture are sufficient descriptors to qualify it as a DES. The prefix *deep* is assigned for eutectic mixtures for which the eutectic point temperature should be lower to that of an ideal liquid mixture,² although the extent of the deviation to ideality required to classify a DES remains a source of debate. The increased melting point depression stems from the stronger intermolecular interactions between the DES components relative to those present in the pure compounds, be those hydrogen bonding³ or others.^{4,5} The most robust evaluation if a system is indeed a DES or a simple eutectic mixture remains through the determination of the phase diagram.

In a recent published work, Busato et al. investigate, via a range of experimental and computational techniques, the mixture composed of butylated hydroxytoluene (BHT) and L-menthol (MEN) for a single composition of $x_{\text{BHT}} = 0.25$.⁶ The results from the different techniques are coherent and indicate an increased self-segregation between the components. However, we disagree that these findings “challenge the fundamental definition of DESs” or that “apolar–apolar attraction might be the driving force” for DES formation. Unfortunately, the phase diagram is not reported to support these claims.

We decided to complement existing literature data on the BHT + MEN phase diagram with our own experimental measurements. The obtained phase diagram shown in Figure 1 (i) presents two eutectic points for $x_{\text{BHT}} \sim 0.24$ and 0.37 and (ii) suggests the formation of two cocrystals with approximate MEN:BHT stoichiometries of 2:1 and 1:1, although this requires further investigation. If the latter is confirmed, it indicates that BHT does engage in limited hydrogen bonding with MEN contrary to the reported findings.⁶ Furthermore, at

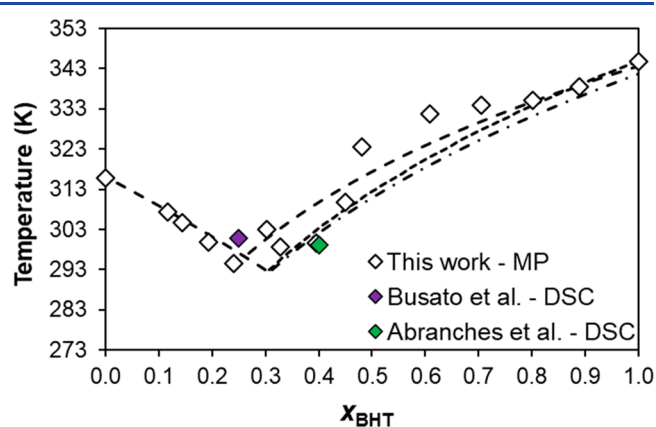


Figure 1. (A) Experimental solid–liquid equilibrium phase diagram of the BHT + MEN system. The dashed line represents the ideal solid–liquid phase diagram, including for three different reported melting enthalpies and temperatures of BHT. After preparation, samples were left to recrystallize for 1 week. Data were measured using an automatic glass capillary device model M-565 from Buchi, with a temperature resolution of 0.1 at 0.1 K min^{−1} or taken from refs 3 and 6 (MP, melting point method; DSC, differential scanning calorimetry). Melting properties of MEN and BHT were taken from refs 7 and 8, respectively.

the studied composition of $x_{\text{BHT}} = 0.25$ by the authors, a positive deviation to ideality is observed (assuming no cocrystal formation) that is consistent with the reported self-aggregation and poor intermixing of the components. By all accounts, the system of BHT + MEN cannot be classified as a *deep* eutectic solvent, and therefore, inferences derived from this system as to new mechanisms for DES formation must be nuanced. Extrapolating results for one mixture point across the entire compositional range can lead to erroneous conclusions as even apparently simple systems present a complex phase diagram.

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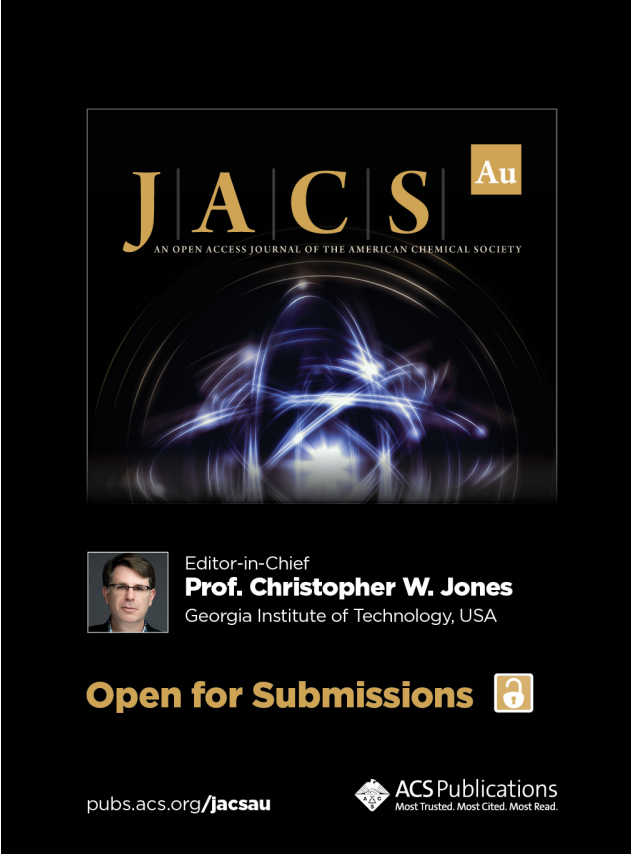
<https://pubs.acs.org/10.1021/acssuschemeng.2c02985>

Notes


The author declares no competing financial interest.


REFERENCES

- (1) Hansen, B. B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J. M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B. W.; Gurkan, B.; Maginn, E. J.; Ragauskas, A.; Dadmun, M.; Zawodzinski, T. A.; Baker, G. A.; Tuckerman, M. E.; Savinell, R. F.; Sangoro, J. R. Deep Eutectic Solvents: A Review of Fundamentals and Applications. *Chem. Rev.* **2021**, *121* (3), 1232–1285.
- (2) Martins, M. A. R.; Pinho, S. P.; Coutinho, J. A. P. Insights into the Nature of Eutectic and Deep Eutectic Mixtures. *J. Solution Chem.* **2019**, *48* (7), 962–982.
- (3) Abranches, D. O.; Martins, M. A. R.; Silva, L. P.; Schaeffer, N.; Pinho, S. P.; Coutinho, J. A. P. Phenolic Hydrogen Bond Donors in the Formation of Non-Ionic Deep Eutectic Solvents: The Quest for Type v Des. *Chem. Commun.* **2019**, *55* (69), 10253–10256.
- (4) Peloquin, A. J.; McCollum, J. M.; McMillen, C. D.; Pennington, W. T. Halogen Bonding in Dithiane/Iodo fluorobenzene Mixtures: A New Class of Hydrophobic Deep Eutectic Solvents. *Angew. Chemie Int. Ed.* **2021**, *60* (42), 22983–22989.
- (5) Abranches, D. O.; Schaeffer, N.; Silva, L. P.; Martins, M. A. R.; Pinho, S. P.; Coutinho, J. A. P. The Role of Charge Transfer in the Formation of Type I Deep Eutectic Solvent-Analogous Ionic Liquid Mixtures. *Molecules* **2019**, *24* (20), 3687.
- (6) Busato, M.; Mannucci, G.; Di Lisio, V.; Martinelli, A.; Del Giudice, A.; Tofoni, A.; Dal Bosco, C.; Migliorati, V.; Gentili, A.; D'Angelo, P. Structural Study of a Eutectic Solvent Reveals Hydrophobic Segregation and Lack of Hydrogen Bonding between the Components. *ACS Sustain. Chem. Eng.* **2022**, *10*, 6337–6345.
- (7) Chickos, J. S.; Garin, D. L.; Hitt, M.; Schilling, G. Some Solid State Properties of Enantiomers and Their Racemates. *Tetrahedron* **1981**, *37* (12), 2255–2259.
- (8) Acree, W.; Chickos, J. S. Phase Transition Enthalpy Measurements of Organic and Organometallic Compounds and Ionic Liquids. Sublimation, Vaporization, and Fusion Enthalpies from 1880 to 2015. Part 2. *J. Phys. Chem. Ref. Data* **2017**, *46*, 013104.



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