C-P144. Tendencies of Solid Phase Formation in Deep Eutectic Solvents of Betaine and Xylitol

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Deep eutectic solvents (DES), formed from Lewis or Brønsted acids and bases [1], often have excellent fluidity. Natural DES from betaine and xylitol, which are solids when pure, may turn liquid if mixed and then show promising biocatalytic performance [2]. This report studies the effects of their ratios on phase separation.

Mixtures were heated to 160℃ or until melting, but those with 50% wt. or more betaine did not melt fully. Molten samples were brought to room temperature for 1 hr and, if still clear, cooled down to ~-20℃. No clouding could be observed in 4 hrs of freezing. Then samples were thawed to room temperature and inspected for phase separation daily. Gradually, solids began to form on the surface of all mixtures. Approximate volume of solids was evaluated visually and durations were recorded when they exceeded 5% and 20% vol, fig. 1.

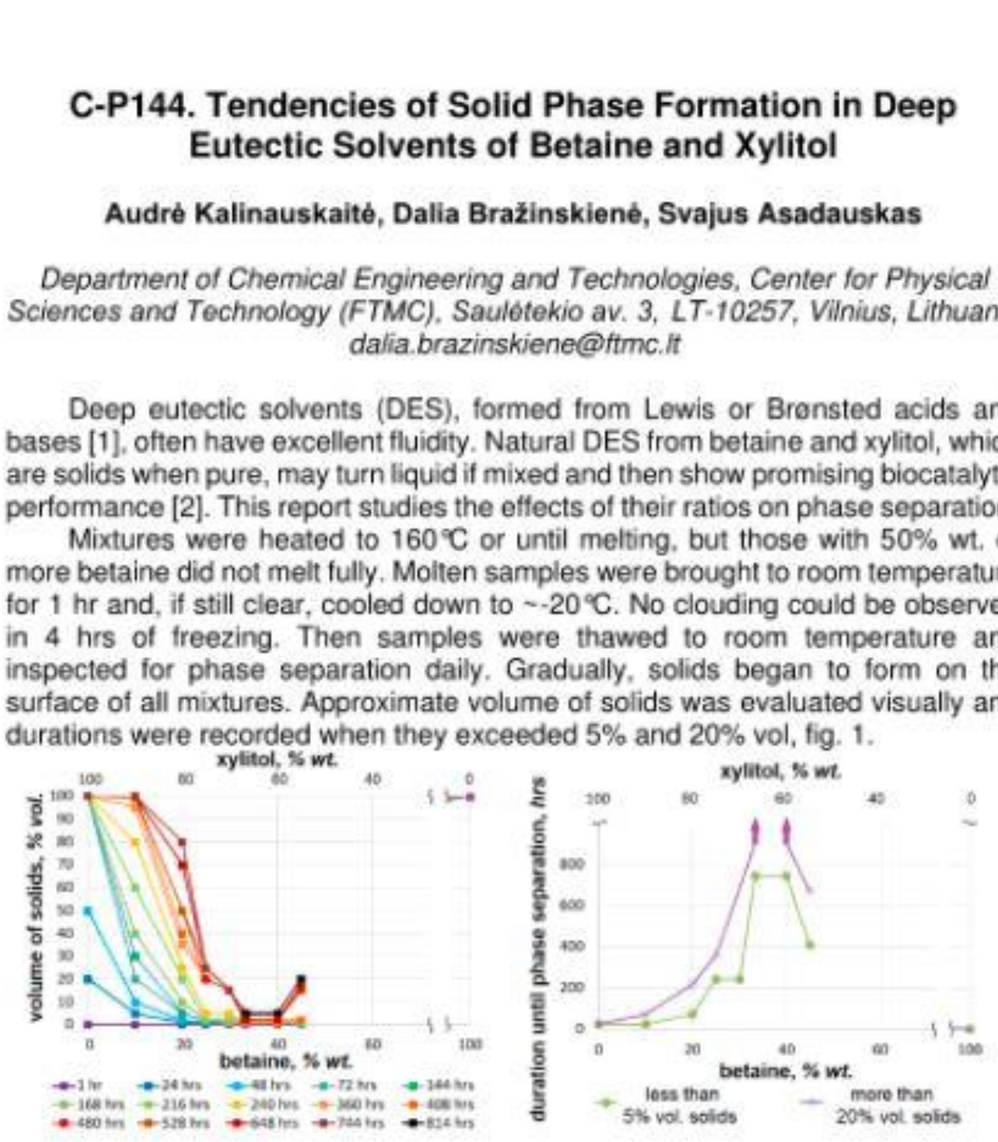

Fig. 1. Extent of solid phase formation in betaine+xylitol mixtures, stored at room temperature (left) and storage durations, needed to reach 5% or 20% solids (right).

Evidently, betaine (m.p. 300℃+) and xylitol (m.p. ~95℃) mixtures with 60-65% wt. of latter can liquefy without any chemical reaction and retain fluidity quite long. Mixtures outside this ratio are not as stable and might form excessive solids.

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Keywords: *deep eutectic solvent, crystallization, cloud point.*

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2. A. E. Delorme et al. *International Journal of Biological Macromolecules* **163** p. 919-926 (2020)

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August 26, Thursday

Chairperson – Donats Erts

8:30 – 9:00	**Registration**
9:00 – 9:45	**Witold Brostow** (University of North Texas, United States of America) **Fire Resistance of Materials**
9:45 – 10:15	**Rynno Lohmus** (University of Tartu, Estonia) **How to Use Wood as a Material More Efficiently?**
10:15 – 10:30	**Coffee break**
10:30 – 11:15	**Ashok Vaseashta** (International Clean Water Institute, United States of America) **Nanofibers of High-Performance Electret Polymers for Tactile Sensing and Wearable Electronics**
11:15 – 12:00	**Azhar Ariffin** (University Malaya, Malaysia) **Carbazole-Based Organic Compounds in Organic Light Emitting Diodes, OLED, Applications**
12:00 – 12:15	**Coffee Break**
12:15 – 13:15	**Morten Madsen** (University of Southern Denmark, Denmark) **Metal Oxide Interlayers for Scalable Organic and Perovskite Solar Cells**
13:15 – 15:00	**Break**
15:00 – 18:30	**Poster Sessions** *Chairperson – Tomas Tamulevičius* 15:00 – 15:45 Poster Session A 15:55 – 16:40 Poster Session B 16:50 – 17:35 Poster Session C 17:45 – 18:30 Online Poster Session
18:45 – 19:15	**Best Poster Awards and Conference photo**

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Tendencies of Solid Phase Formation in Deep Eutectic Solvents of Betaine and Xylitol

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INTRODUCTION

Deep eutectic solvents (DES), formed from Lewis or Brønsted acids and bases [1], often have excellent fluidity. The charge delocalization during hydrogen bonding between the hydrogen bond acceptor (HBA) and the hydrogen bond donor (HBD) decreases the melting point of the mixture, Fig. 1, relative to the melting points of the individual components [2]. For example, betaine melts at ~300°C and xylitol melts at ~95°C, but some of their mixtures can melt at much lower temperatures.

DES can find utilization in metal processing [1], organic reactions [3] and extractions [4], and electrochemistry [5]. Natural DES from betaine and xylitol, which are solids when pure, may turn liquid if mixed and then show promising biocatalytic performance [6]. This report studies the effects of their ratios on phase separation.

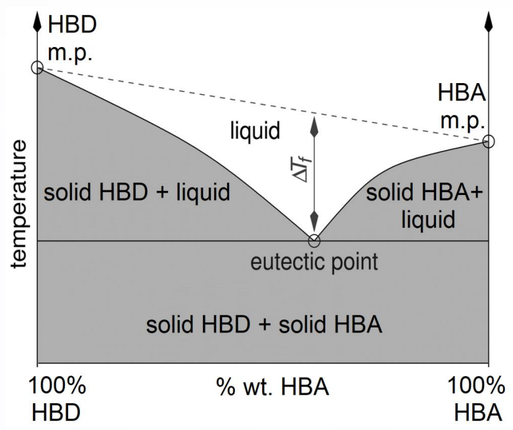


Fig.1 Schematic representation of a eutectic point on two-component (HBA and HBD) phase diagram under thermodynamic equilibrium.

MATERIALS

Xylitol, $HOCH_2(CHOH)_3CH_2OH$ (Fig. 2) is solid at room temperature, but it can be heated and supercooled to produce a highly viscous liquid. It gradually solidifies due to activation energy required for the conformational changes and its crystals grow slowly at ambient temperature [7]. Supercooling effects should also be expected in xylitol blends. Instead of m.p. measurements, it is more reasonable to monitor freezing and crystallisation trends. Betaine, Fig. 3, is a quaternary ammonium zwitterion which is biodegradable, non-toxic and can be extracted from natural resources [8]. Therefore betaine-based DESs have wide perspectives [9].

EXPERIMENTAL

Mixtures were heated to 160°C or until melting, but those with 50 % wt. or more betaine did not melt fully. Molten samples were brought to room temperature for 1 hour. Since the crystal growth was slow, melted mixtures, if still clear, were cooled down to ~-20°C. No clouding could be observed in 4 hours of freezing, implying supercooling trends. Then samples were thawed and inspected daily for phase separation at room temperature. Gradually, solids began to form on the surface of all mixtures. Approximate volume of solids was evaluated visually and durations were recorded when they exceeded 5% and 20% vol. Melting points of DESs were not measured either because betaine-rich mixtures stayed solid up to 160°C or because supercooled xylitol blends remained liquid after freezing to -20°C.

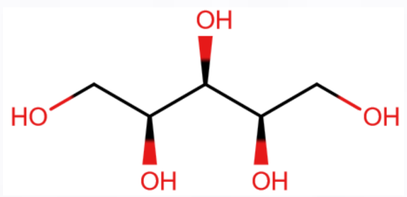


Fig. 2 Xylitol (HBD)

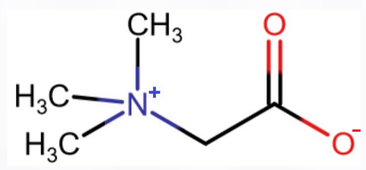


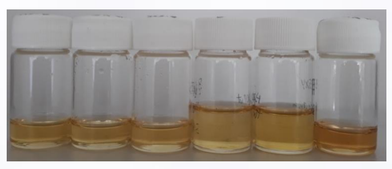
Fig. 3 Betaine (HBA)

Fig. 4 Appearance of DES blends during various stages of melting, cooling and phase separation in storage

Initial appearance of pure betain, xylitol and their blend

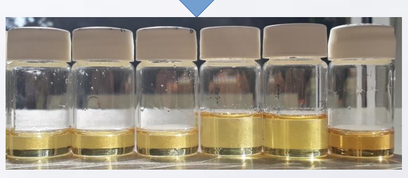
Heated DES at 160°C

Some DES melt fully



Cooling down from 160°C

Supercooling at -20°C



Storage at room temperature

Gradual solids formation

RESULTS

Variation of betaine/xylitol ratio in DES resulted in different liquefaction rates when heating and crystallisation rates after supercooling. Since the blends with 50% wt. or more betaine did not fully melt at 160°C, their crystallization was not further studied. Due to supercooling, pure xylitol remained fully liquid for several hours, then began crystallizing and reached 100% solids in 72 hrs. Its blends with increasing percentage of betaine retained liquidity progressively longer, Fig. 5. The trend is very evident that in the vicinity of 40/60 w/w ratio of betaine/xylitol the blends have remarkable fluidity. Nevertheless, some crystallization takes place even in those DES. The 40/60 blend produced 5% vol. solids in 744 hrs, but has not reached 20% solids beyond 2200 hrs, Fig. 6. It can be suspected that the amount of entrained humidity has a significant impact on solidification trends, however, a separate study would be needed to assess the effects of moisture quantitatively.

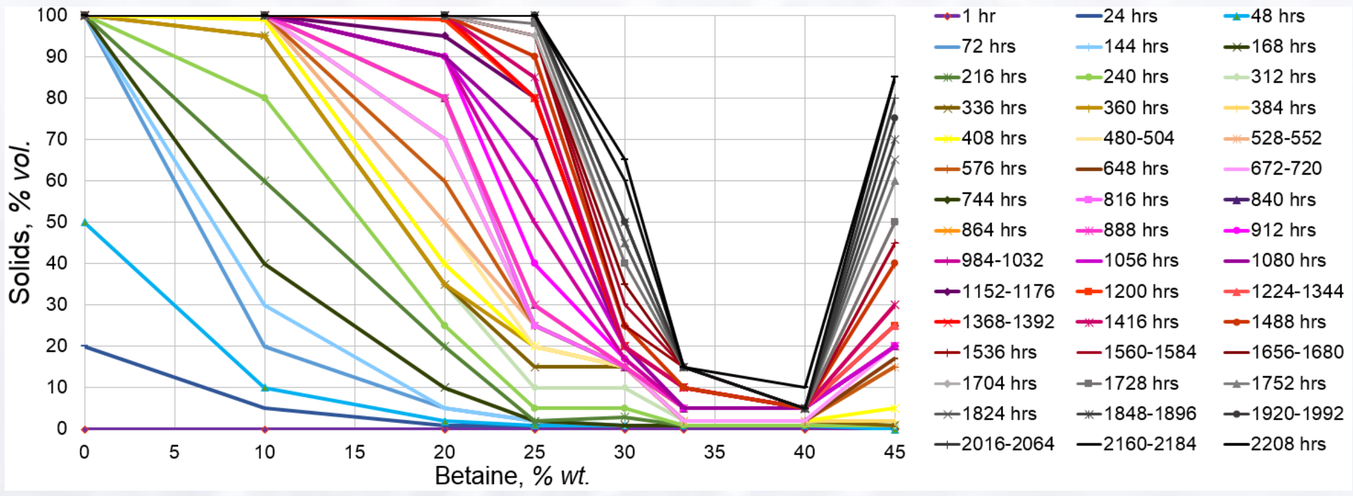


Fig. 5 Effects of betaine contents on solids formation in supercooled DES.

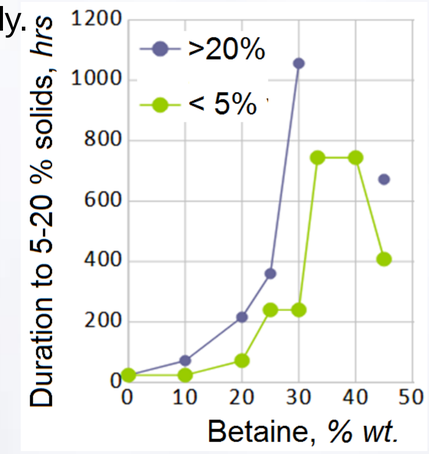


Fig. 6 Durations needed to reach 5 or 20 % vol. solids during phase separation

CONCLUSIONS

- Betaine mixtures with 60-65% wt. xylitol can liquefy without any chemical reaction and retain fluidity for prolonged durations. Mixtures outside this ratio are not as stable and might form excessive solids.
- Measurement of melting or freezing points might not be appropriate when supercooling effects are significant. Solids formation should be monitored.
- Formation of small amounts of solids on the DES surface could not be avoided. Effects of humidity should be considered.

ACKNOWLEDGMENTS

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