

## VISCOMETRY, VOLATILITY AND STABILITY OF DEEP EUTECTIC SOLVENTS FROM BETAINE

*D. Bražinskienė, T. Matijošius, S. Asadauskas \**

State Research Institute Center for Physical Sciences & Technology (FTMC), Lithuania

**Abstract:** Deep eutectic solvents can be formed from solids without any reaction or ionic exchange. Recently, natural deep eutectic solvents (NADES) are gaining popularity in extraction, lubrication or cooling, in particular betaine-based ones. A series of betaine formulations with xylitol and glycerol as H-bond donors were prepared and tested. A blend of betaine and glycerol at 1:2 wt. ratio recorded 456 mm<sup>2</sup>/s and 25.2 mm<sup>2</sup>/s at 40°C and 100°C, while that of betaine and xylitol was much more viscous with 234 mm<sup>2</sup>/s at 100°C. Their volatility was studied by exposing thin films of NADES on steel and aluminum surfaces at 90°C. Vaporization rates depended on the molecular weight of H-bond donors and their thermal/oxidative resistance. Initially, both combinations showed similar lack of volatility, but in long term testing xylitol-based NADES turned out significantly less volatile than those of glycerol. Although viscosities were higher than those of conventional organic solvents, broad viscometric range and satisfactory stability imply many promising applications for NADES.

Keywords: Viscosity, phase separation, oxidative degradation

### 1. INTRODUCTION

Users of fossil-based and synthetic fluids in technical, automotive, agricultural, medical and many other fields are increasingly interested in switching to renewable and environmentally friendly alternatives. Recently, a new option has been provided by reporting [1] the development of a new class of liquids as Natural Deep Eutectic Solvents (NADES). It was established that these can be formed from two or more bio-derived compounds without the need for any chemical reaction or ionic exchange. One compound acts as a hydrogen bond donor, while another behaves as an H-bond acceptor. At least one must be a solid, however, otherwise there would be no eutectic effect. After mixing, the solids should eventually liquefy due to H-bond transformations and de-crystallization. Recently, NADES are gaining popularity in many applications, especially in extraction. They often demonstrate extraordinary solubilizing power and have already been used in extracting proteins, DNA, saccharides or metabolites. Lubricants, cosmetics and adhesives provide another avenue for NADES utilization, where they have already been employed for additive stabilization and dispersability.

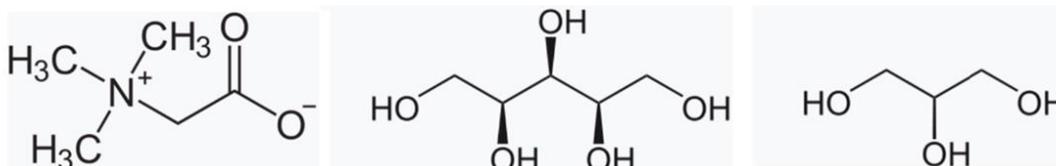
Betaine-based NADES are among the most widespread, assuring high bio-derived contents, readily available feedstock and very low crystallization temperatures. One major advantage is provided by their regulatory status, because NADES components are still individual chemical compounds, despite very different properties of their blend. Existing regulations (REACH, TSCA, OSHA, etc.) apply to the specific chemical compounds, but not to NADES, although the latter might provide technical properties, which are dramatically different from those of their individual constituents. Betaine, being a widely recognized compound with well-perceived regulatory status can act as an effective H-bond acceptor in formulating NADES. For H-bond donors, a variety of environmentally friendly bio-derived alcohols and acids can be used. This gives formulators some additional flexibility without the need to worry about toxicological, environmental or other regulatory implications. Once diluted in water, NADES rapidly lose the exclusivity of their technical advantages because then they simply dissolve in aqueous media. Therefore, the environmental fate of NADES is essentially the superposition of environmental impacts of the H-bond donor and the H-bond acceptor individually. Regarding H-bond donors, in this study, the focus was devoted to xylitol and glycerol. Viscosities and stability of their blends with betaine were compared to general trends of conventional solvents and oils, such as vegetable oils, their esters, organic solvents, mineral oils and other petroleum fractions.

## 2. EXPERIMENTAL

Although this study involved many tests, which are widely recognized, some experiments were custom-designed for this investigation. Therefore, materials and procedures are described in the below subchapters by devoting much more detail to the newly developed methodologies.

### 2.1. Materials

Suppliers of research chemicals provided the main materials for NADES formulation. Betaine (from Sigma-Aldrich) had 99.3% purity by titration, as certified by the supplier. Its melting point (m.p.) could not be determined, because betaine decomposes above 200°C. Xylitol (from Roth) had 99% purity and certified m.p. of 94°C. Glycerol (from TCI Chemicals) was certified at 99% purity. Molecular structures of the tested materials are shown in Figure 1.



**Figure 1.** Molecular composition of betaine (left), xylitol (center) and glycerol (right).

Betaine and xylitol were solids during the storage at room temperature, while glycerol was liquid. Acetone and isopropanol of technical grade were used as cleaning solvents. Entrainment of ambient air was limited by capping the bottles as often as possible and purging them with dry N<sub>2</sub> periodically.

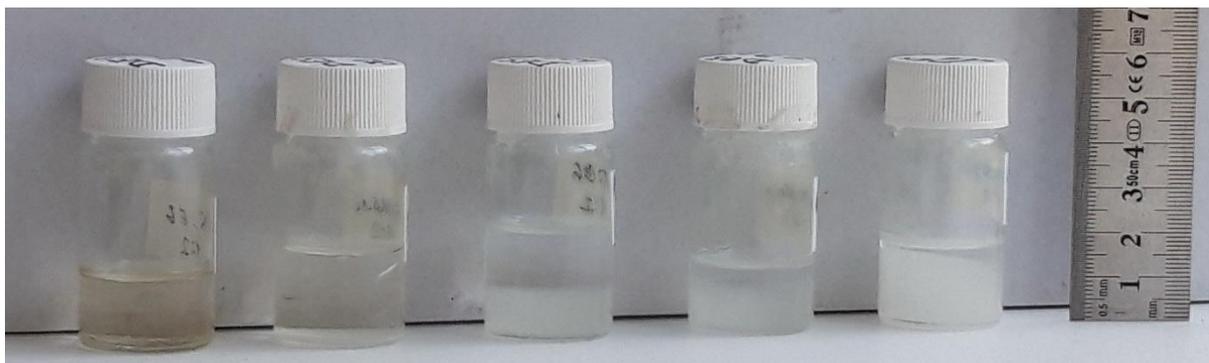
### 2.2. Preparation of NADES

The components, which were used for NADES formulation, had been stored in carefully capped containers to limit any entrainment of ambient air. The containers were open only briefly immediately before the blend preparation to take the components out for weighing and subsequent mixing. Clear glass scintillation vials of 20 mL capacity were used, measuring H= 60 mm and OD = 25 mm. The components were poured directly into the vials and the mix was vigorously stirred for 10-20 s with a spatula. Then the vial was immediately capped and later placed into the convection oven at 130°C or other specified temperature, if indicated separately. The vials were periodically taken out of the oven, typically once an hour, and shaken vigorously without removing the cap to assure some agitation in the blend. The heating duration was set at 3 hrs, unless longer heating was needed for the powders to blend into NADES. In this report, longer heating durations are specifically indicated for every case.

### 2.3. Procedures for fluidity tests

Fluidity experiments were performed by measuring viscosities of prepared NADES samples and monitoring their precipitation tendencies during storage. The vials with the samples were kept at room temperature and periodically taken out from the storage for the evaluation of precipitate formation. The phase separation was evaluated visually by lining the vials up to the ruler and estimating the amount of volume, occupied by the precipitate, as shown in Figure 2. Although not all photographed samples are based on the chemicals of this study, determination of their precipitation trends followed the same measurement procedures as for the betaine-based NADES.

In many samples the precipitate was not very compact and contained significant amounts of the original liquid phase. Occasionally, a plane between the separate phases was not flat or horizontal. No additional attempt was made to separate the phases, such as centrifuging or sonication, so the determination of the exact amount of solids was not possible using this method. The ruler was used to measure the phase thicknesses from several sides of the vial and an arithmetic average was calculated to determine the volume, occupied by the precipitate. Despite these approximations, it could still be established whether the sample was stable (0% precipitate) or precipitation was minor (0-5% precipitate), medium (5-20%) or progressively higher intensity, as indicated by the percentage intervals in Figure 2. Repeatability of this procedure was good with all reruns yielding similar amounts of the solid phase, which only varied somewhat in the shapes of the precipitate, but not that much in its volume. Such semi-quantitative estimation of the phase separation still gave a reasonable assessment of the precipitation tendencies.



**Figure 2.** Visual determination of the precipitation intensity in five NADES samples from the left: 0%, 0-5%, 20-50%, 50-80% and 80-90%.

Viscosities of NADES samples were measured by using an adapted ASTM D445 procedure with Cannon-Fenske capillary viscometers from Fungilab (Netherlands). Temperatures of 40°C or 100°C were maintained within  $\pm 0.2^\circ\text{C}$ . Only kinematic viscosities were measured during this study. Some viscosity data was extracted from literature sources, including dynamic viscosities and densities. When comparing the literature data with the current experimental results, kinematic viscosities were used as the basis. If needed, they were calculated by dividing the dynamic viscosity by density.

#### **2.4. Volatility measurements**

A long-term vaporization of NADES samples was measured using a thin film method under the conditions of a severe oxidative stress. The procedures, described in detail previously [2], [3] employed placing the sample on the surface of a metal coupon and heating in a forced-draft oven HCP-108 (from Memmert GmbH) at 90°C. Analytical balance ALJ-160-4NM (from Kern Analytical Instruments GmbH) was used to weigh the coupons with or without the sample film at  $\pm 0.1$  mg accuracy. The coupons were cut in-house from low carbon steel (>99% Fe) or aluminum alloy and their surface was disc-like of 16 – 19 mm OD. The samples were added onto their surface to produce a film of  $500 \pm 20$   $\mu\text{m}$  thickness. This was ensured by weighing each coupon before and after the sample addition.

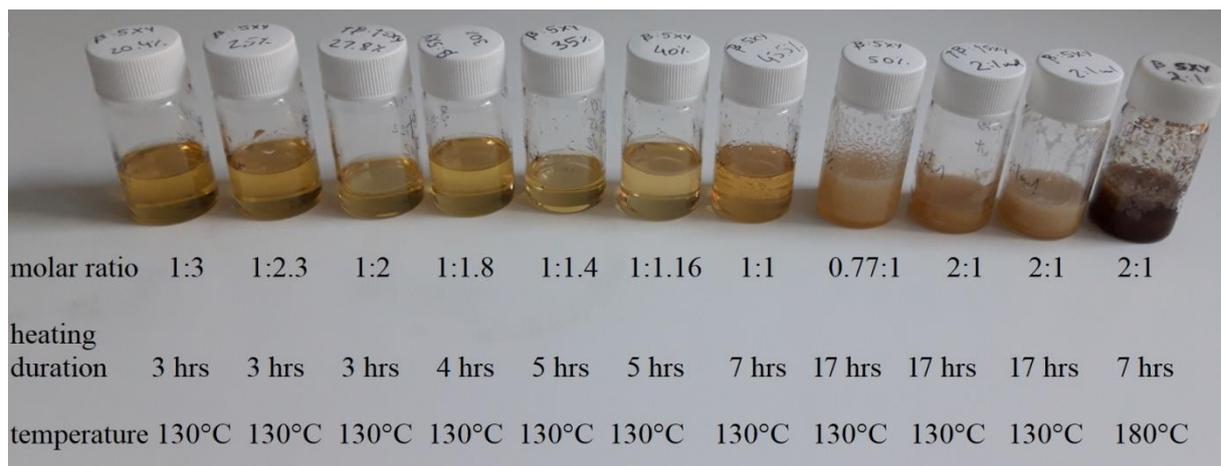
Periodically, the coupons were taken out of the oven and weighed to determine weight losses. In some cases weight gains were detected, which could be a result of oxidation. Their values were listed as negative losses. Oxidation could also affect the metal coupon itself. Previous studies showed that weight gain on uncoated areas of the steel surface could result in 0.2% increase of the sample weight reading. Such increase was detectable, but could be considered negligible for the purposes of this study. Aluminum surface was less sensitive to oxidation and no weight gain was detected in its case.

### **3. RESULTS AND DISCUSSION**

Viscometry results are discussed in a designated subchapter, while stability results and discussion are segregated between the two subchapters on phase separation and thermal degradation. The latter also includes the findings on volatility aspects.

#### **3.1. Composition effects on liquefaction and phase separation**

Not every formulation of betaine and xylitol may constitute NADES. In order to qualify, the sample must be liquid by the definition, since NADES abbreviation includes a term “solvent”. Since both betaine and xylitol represent solids at room temperature, immediately after mixing they remain powders, lumps or other solid particulates. Either long-term storage or heating are necessary for their de-crystallization to become intensive enough, resulting in the formation of a liquid phase. In this study, heating duration was varied from 3 to 17 hrs in order to observe the liquefaction of various betaine-xylitol formulations. Heating at 130°C was sufficient to liquefy xylitol-rich formulations. However, many samples could not turn liquid even at 180°C, see Figure 3.



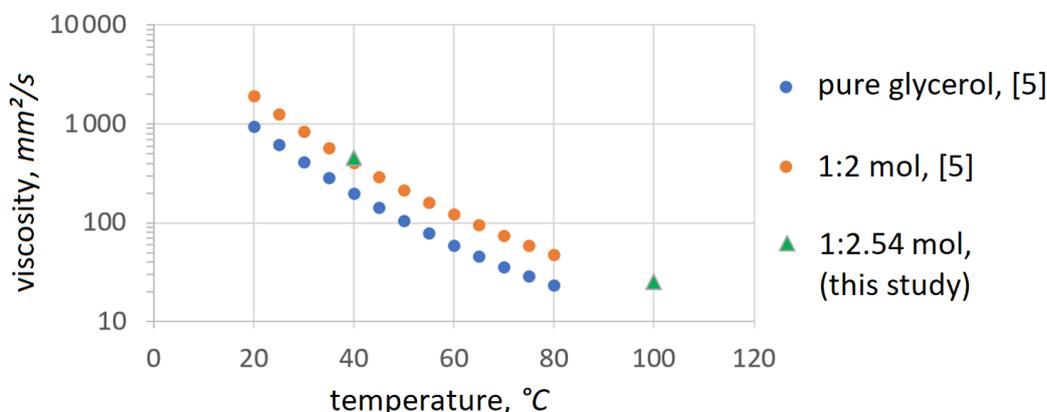
**Figure 3.** Appearance of various betaine and xylitol mixtures after heating at different temperatures and durations. Photographed after cooling to room temperature.

It appears that higher amount of betaine inhibits the liquefaction of the mixture. At 2:1 mol betaine excess, the mixture could remain fully liquid only when heated. When cooled to room temperature, this mixture produced 50-80% solids. The formulation at 1:1 mol ratio was much more liquid-like and the solids amounted to less than 5% after cooling. At least 1:1.16 mol excess of xylitol was needed to achieve a solids-free NADES at room temperature. Even then, detectable amounts of precipitate would still appear during its storage. Precipitate formation trends had been analyzed in much greater detail previously [4]. It was established that 1:1.54 mol blend of betaine and xylitol, which corresponds to 1:2 wt. ratio, produces NADES of excellent long-term fluidity with only minor precipitate, likely due to moisture entrainment. Super-cooling effects were also noted for xylitol, whose betaine-free samples remained mostly liquid at room temperature for nearly 2 days after heating to 130°C despite certified m.p. of 94°C.

Betaine blends with glycerol showed substantially better fluidity, most likely due to glycerol's m.p. being below room temperature. However, at 1:1 mol ratio their mixture could not remain liquid during storage at room temperature. As in the case of xylitol, 1:2 wt. excess of glycerol, which corresponds to 1:2.54 mol ratio, assured sufficient long term fluidity with essentially zero precipitate.

### 3.2. Viscometry of betaine-based NADES with xylitol and glycerol

Viscosity is among the most important characteristics of liquids in many applications, such as adhesives, extraction solvents, lubricants, etc. Previous reports [5], [6] have already looked into viscometric behavior of some betaine-based NADES to some extent, including the one of 1:2 mol betaine : glycerol. In this study, viscosity of a similar formulation was measured and compared to the data from other researchers, see Figure 4.



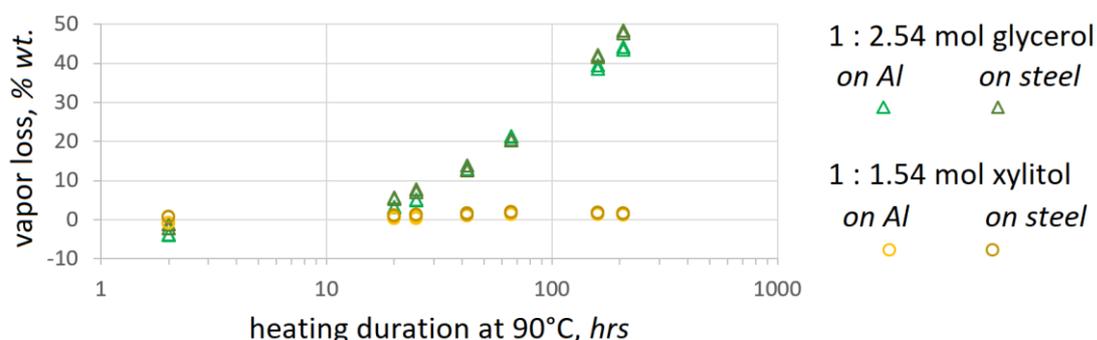
**Figure 4.** Temperature dependence of kinematic viscosities for betaine : glycerol blends. Values for pure glycerol and 1:2mol betaine:glycerol formulation were calculated from the data reported elsewhere [5].

Both formulations showed similar viscosities at 40°C, which meets expectations, so the measurement of 456 mm<sup>2</sup>/s confirms the validity of both methodologies. Viscosity measurement of 25.2 mm<sup>2</sup>/s at 100°C seems to fit the logarithmic trend of temperature dependence quite well also. Viscosity Index of 69 is inferred from these measurements. Compared to conventional fluids, viscometric behavior of this particular NADES is similar to that of bright stock, i.e. solvent refined heavy mineral oil, whose viscosity typically ranges from 20 to 50 mm<sup>2</sup>/s at 100°C. It should be noted that these viscosities are much higher than those of conventional organic solvents, such as isopropanol, naphtha and fatty acid methyl esters or even vegetable oils. The latter rarely have viscosity above 10 mm<sup>2</sup>/s at 100°C.

Viscosities of NADES from betaine : xylitol were even higher. It was just not possible to measure those using on-site capillary viscometers at 40°C. Therefore, only the measurement of 234 mm<sup>2</sup>/s at 100°C was recorded for the samples of 1:1.54 mol betaine : xylitol. Such extreme viscosity is nowhere close to any solvents and approaches that of asphaltene-rich petroleum fractions. Please note that analogies with bright stock and other oils are just viscometric, because other properties, like color, odor, solvency, stability, etc. are very different between those materials and betaine-based NADES.

### 3.3. Long-term volatility of betaine-based NADES

Liquids can volatilize thermally because of two main reasons. First, they undergo thermodynamic phase transition when liquid turns into vapor. The rate of such phase transition mainly depends on temperature and convection, i.e. extent of vapor saturation. The second driving force behind the emission of volatile losses is thermal and chemical decomposition into compounds of lower mol. wt. which can evaporate easier. In technical applications, the decomposition aspects can be very important, especially in adhesives, coatings or lubricants. Therefore, long term vaporization trends of betaine-based NADES using 1:1.54 mol and 1:2.54 mol excess of xylitol and glycerol respectively, were compared at 90°C. These molar ratios reflect the same weight ratio of 1:2 for both combinations. A thin film methodology, originally developed for lubricant testing, was employed using the film thickness of 500 µm and exposure to air. Due to unrestricted availability of oxygen in air, the NADES films underwent quite significant oxidative degradation. Thermal and oxidative stress led to additional generation of lower mol. wt. products, as shown in Figure 5.



**Figure 5.** Volatile losses due to thermal and oxidative degradation of NADES films on steel and aluminum surfaces for 1: 2.54 mol betaine-glycerol and 1:1.54 mol betaine:xylitol samples.

Glycerol-containing sample showed much higher rate of volatile emissions. It could be related to lower mol. wt. of glycerol (92.1 g/mol), compared to that of xylitol (152.1 g/mol) or betaine (117.1 g/mol). However, the difference is surprisingly large, especially during the late stages of the test. This might be explained through poorer oxidative stability of glycerol compared to xylitol. In addition, after 2 hrs of heating the glycerol-containing sample gained weight, as opposed to the xylitol-containing sample. Considering that weight wise both samples contained the same amount of betaine, this implies that glycerol was absorbing oxygen much faster than xylitol. Slight catalytic effect of surface material can be observed also, because the samples on steel surface consistently showed somewhat higher vapor losses. Steel is less inert than Al, which can also contribute to the rate of oxidation.

Therefore, volatility of NADES should also be evaluated under long-term thermal and oxidative stress conditions. During short-term testing, e.g. within 2 hrs, the results might be quite misleading, compared to long-term trends. Such paradox is evident when considering the volatile emission data for betaine-based NADES with glycerol and xylitol.

#### 4. CONCLUSIONS

In this investigation, a series of betaine:xylitol and betaine:glycerol mixtures were prepared to observe their liquefaction with heating and phase separation when cooled. The most stable formulations were tested for long-term volatile emissions. Their kinematic viscosities were also measured and compared to the literature reports. Several conclusions could be drawn from the findings.

- Viscosities of betaine-based NADES are much higher than those of typical organic solvents, vegetable oils or their esters, but comparable to viscous mineral oils like bright stock.
- Volatilities of NADES are dependent on mol. wt. of their constituents. Long-term volatile emissions are also strongly affected by their thermal and oxidative resistance.
- Long-term stability under thermal and oxidative stress might be substantially different from that of short-term stability.

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\* Author for contacts: dr. Svajus Asadauskas  
E-mail: svajus.asadauskas@ftmc.lt