

# **Influence of Hydrogen Bond Donor Identity and Intentional Water Addition on the Properties of Gelatin-Supported Deep Eutectic Solvent Gels**

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## ABSTRACT

Deep eutectic solvent (DES) gel electrolytes have recently emerged as promising alternatives to ionic liquid- or water-based gels for “ionic skin” sensor applications. Researchers have also been exploring the effects that varying amounts of water may have on the local hydrogen bonding environment within a few model DES systems. In this study, the physical properties and ionic conductivities of biopolymer (gelatin)-supported gels featuring two established DESs and three DES/water mixture formulations are investigated and compared. The DES/water mixtures are formed by combining choline chloride with one of three organic hydrogen bond donors (HBDs): ethylene glycol, glycerol, or 1,2-propanediol, in a 1:2 molar ratio, together with a controlled amount of water, 25 mol% (approximately 5-6 wt.% water). For the same fixed gelatin content (20 wt.%), DES/water mixture gel Young’s modulus values are found to be tunable based on the organic HBD identity, increasing six-fold from 7 kPa (1,2-propanediol) to 42 kPa (glycerol). Furthermore, large differences are observed in the resulting gel properties when water has been intentionally added to well-studied DESs. Coformulation with water is found to increase ethylene glycol-based DES gel toughness, measured via tensile testing, from 23 to 68 kJ/m<sup>3</sup> while simultaneously boosting gel room temperature ionic conductivity from 3.3 to 5.2 mS/cm. These results highlight the multiple roles that controlled amounts of water-in-DES can play within gelatin-supported DES/mixture gel electrolytes, such as influencing gelatin self-assembly and reducing local viscosity to promote facile ion transport.

## INTRODUCTION

Intimate interfacing between flexible devices and biological tissue is essential for precise, continuous monitoring of underlying biophysical activity. In particular, smart sensing “skin” requires mimicry of human skin-like capabilities, such as withstanding repetitive mechanical deformation during bending and stretching, all while maintaining conformal contact with the biological tissue. “Ionic skins” comprised of salty hydrogels<sup>1,2</sup> or ionogels<sup>3,4</sup> are optically transparent, mechanically compliant composites that have emerged as potential platforms for this kind of biomimetic device. However, the electrolytes used in these systems are currently limited either by poor stability in air due to evaporation in the case of aqueous electrolytes, or by high cost and toxicity in the case of many ionic liquids.

Deep eutectic solvents (DESs) are liquid mixtures at or near a eutectic composition that exhibit a high degree of nonideality due to significant attractive hydrogen bonding interactions between their constituent components. Archetypical DESs are binary combinations of a quaternary ammonium salt, such as choline chloride (ChCl), and a suitable hydrogen bond donor (HBD) that induces charge delocalization to produce a significantly depressed eutectic melting point.<sup>5</sup> Importantly, this class of ion-dense electrolytes possesses many of the crucial merits of ionic liquids, such as an ultralow volatility and wider electrochemical stability window compared to aqueous electrolytes, together with a biofriendly nature and lower cost.<sup>5–7</sup>

Researchers have recently started to investigate more closely the role of water within DES systems, as DES components are often hygroscopic, to determine whether it behaves like bulk water on the molecular level or if it can play the role of an additional HBD.<sup>8–10</sup> It has already been reported that H<sub>2</sub>O may act as a co-HBD at low H<sub>2</sub>O concentrations within hydrated DES mixtures;<sup>9</sup> this has the added benefit of reducing the mixture viscosity, which improves both

ionic conductivity and liquid processability.<sup>11</sup> To date, most studies have focused on the DES dubbed reline, a 1:2 molar ratio mixture of ChCl:urea,<sup>8–10</sup> with some studies of the 1:2 molar ratio mixture of ChCl:glycerol (Gly) and the 1:2 molar ratio mixture of ChCl:ethylene glycol (EG) DESs.<sup>12–14</sup> Across computational and experimental studies alike, researchers have demonstrated the existence of two distinct regimes: one in which the DES/H<sub>2</sub>O mixture exhibits typical DES characteristics (at low water concentrations), and another in which water has diluted the DES to the point where characteristic DES motifs can no longer be observed.<sup>8–10,12,13</sup> To our knowledge, however, there have not yet appeared any studies of the effects of water on polymer-supported gel electrolytes featuring a low water concentration DES/H<sub>2</sub>O mixture.

Our group recently reported the creation of a biopolymer-supported DES gel electrolyte (1:2 ChCl:EG DES gelled using gelatin from porcine skin), which we employed in a capacitive tactile sensor.<sup>6</sup> The DES gel exhibited remarkable stretchability and toughness unparalleled by its hydrogel analogue. Stark differences observed in the mechanical properties of DES gels versus hydrogels with the same gelatin content highlight the crucial role of the solvent during the gelation process. We postulated that these differences were due to an increase in the number of dynamic (nonhelical) crosslinks, driven by the presence of ChCl in the DES, in addition to changes in the self-assembled gelatin triple helices that formed within the EG versus H<sub>2</sub>O HBD environments.<sup>6</sup> Although this was the first report to demonstrate the application of gelatin-supported DES gels in nonvolatile, skin-like sensors, there is still a need for a greater fundamental understanding of how the individual DES components may dictate gelatin self-assembly during the *in situ* gelation process.

In this work, we have investigated how HBD selection and the presence of small, controlled amounts of water influence both the room temperature ionic conductivity and physical properties

of DES/H<sub>2</sub>O mixtures and their corresponding freestanding, gelatin-supported gel electrolytes. Five different formulations of ChCl-based mixtures are prepared using EG, Gly, 1,2-propanediol (PD), and water to examine specific HBD effects on the gelatin self-assembly upon cooling from a warm solution (coil-to-helix transition) and how DES/mixture gel properties relevant to ionic skin applications can be tuned. While both the Gly and PD HBDs possess molecular structures similar to EG (see Figure 1), the results of this study reveal that the mechanical properties of gelatin-supported DES/mixture gel electrolytes, such as tensile strain at break, Young's modulus, and toughness, are clearly HBD-dependent. FTIR spectroscopy and thermal analysis are used to probe relative triple helix content and helix length among the various gels. We use these findings to postulate how DES components interact with each other and the gelatin scaffold, thus providing greater insights into gelatin self-assembly within different DESs and DES/H<sub>2</sub>O mixtures. Our enhanced understanding of these systems can enable the improved design of ionic skin mechanical properties to better match those of underlying tissue without modifying the polymer scaffold itself.

## EXPERIMENTAL METHODS

**Materials.** All materials were used as received without further purification. Ethylene glycol (99%, Acros Organics) and glycerol (99%, Alfa Aesar) were purchased from Fisher Scientific. 1,2-propanediol (99.5%) and gelatin from porcine skin (Type A, gel strength ~175 g Bloom) were purchased from Sigma Aldrich. Choline chloride (JT Baker, Baker analyzed reagent) was purchased from Fisher Scientific and stored in a recirculating nitrogen-filled glove box (O<sub>2</sub>, H<sub>2</sub>O < 0.1 ppm) to prevent water absorption from the ambient environment. All other chemicals were stored in the dark prior to use.

**DES/Mixture Formation and Gel Fabrication.** The EG- and Gly-based DESs were formed by mixing ChCl and the respective hydrogen bond donor (HBD) in a 1:2 molar ratio. The DES/H<sub>2</sub>O mixture formulations were created by combining ChCl, the respective HBD, and deionized H<sub>2</sub>O in a 1:2:1 molar ratio. This selected molar ratio resulted in H<sub>2</sub>O contents of approximately 5-6 wt.% within the DES/H<sub>2</sub>O mixtures (Table S1, Supporting Information). All mixtures were stirred vigorously in a sealed vessel on a hotplate set at 90 °C for two hours or until a clear, homogeneous liquid was formed.

To create a gel precursor solution, gelatin was placed in a separate glass vial to which a small volume (approximately one fifth of the total DES/mixture to be added) of room temperature DES/mixture liquid was added to “bloom” the gelatin for improved dissolution. The remaining DES/mixture was heated on a hotplate at 80 °C and subsequently added to the bloomed gelatin vial to create an overall 20 wt.% gelatin solution. This gel precursor solution was stirred on the hotplate at 80 °C for one hour, or until a transparent solution was formed. The warm solution was then poured into silicone or poly(tetrafluoroethylene) (PTFE) molds to define the gel shape and refrigerated at 4 °C in a covered container for at least 24 hours.

**Electrical Characterization.** AC impedance spectra were measured for each liquid and gel formulation in triplicate using a VersaSTAT 3 Potentiostat with a built-in frequency response analyzer (Princeton Applied Research). Gel precursor solutions were poured into custom PTFE cells with gold-coated electrodes and chilled *in situ* at 4 °C for at least 24 hours. AC impedance spectroscopy was performed under ambient conditions (22 °C and 43% relative humidity, RH) over a 1 Hz to 100 kHz frequency range using a 10 mV sinusoidal applied voltage with a 0 V DC offset. The high frequency plateau of impedance values were converted to ionic conductivities

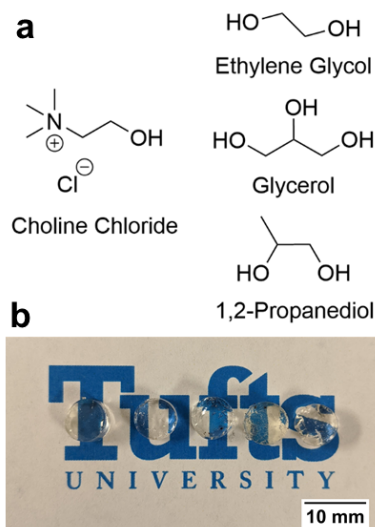
using a constant geometrical factor that was determined via cell calibration with three different neat ionic liquid electrolytes of known ionic conductivities.

**Mechanical Characterization.** Compression and tensile testing of each gel formulation was performed using a RSA III Dynamic Mechanical Analyzer (TA Instruments). For compression tests (see Supporting Information), samples were gelled inside of a cylindrical silicone mold (11.5 mm diameter, 5 mm height) and compressed at a rate of 0.01 mm/s. For tensile tests, samples were gelled inside a rectangular prismatic PTFE mold (4 mm width x 3 mm height x 20 mm length). Gels were manually clamped on both ends to set an initial distance of 10 mm between the instrument clamps. The tensile stretch rate used was 0.1 mm/s.

**Thermal Characterization.** Differential Scanning Calorimetry (DSC) measurements were performed using a TA Instruments Q100 with a nitrogen gas flow rate of 50 mL/min. Samples with masses of 16-19 mg were prepared in aluminum pans. The samples were first heated to 80 °C for 20 min in order to eliminate thermal history effects. Samples were then cooled at a rate of 10 °C/min to 5 °C, held at 5 °C for 60 min, then heated at a rate of 5 °C/min to a final temperature of 80 °C.

**FTIR Spectroscopy.** Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet 6700 FTIR (Thermo Scientific, USA) and a Smart iTX ATR accessory.

## RESULTS AND DISCUSSION



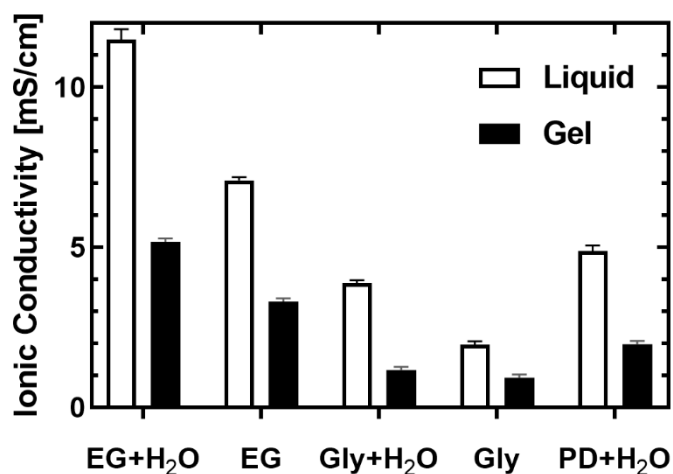
**Figure 1.** (a) Molecular structures of the DES components: choline chloride (ChCl) and the three organic HBDs employed in this study: ethylene glycol (EG), glycerol (Gly), and 1,2-propanediol (PD). (b) Photograph of the five different 20 wt.% gelatin-supported DES/mixture gel formulations investigated (from left to right: EG+H<sub>2</sub>O, EG, PD+H<sub>2</sub>O, Gly+H<sub>2</sub>O, Gly. See text for the details of each formulation).

Five different solutions were prepared by stirring the requisite quantities of ChCl, organic HBD, and water, if included, together on a hotplate until a homogeneous solution was achieved. Figure 1(a) displays the molecular structures of ChCl and the three organic HBDs employed in this study. 1:2 molar ratio mixtures of ChCl:EG and ChCl:Gly were formed (*i.e.* established DESs), as well as 1:2:1 molar ratio mixtures of ChCl:EG:H<sub>2</sub>O, ChCl:Gly:H<sub>2</sub>O, and ChCl:PD:H<sub>2</sub>O. These five DES/mixture formulations are henceforth referred to as EG, Gly, EG+H<sub>2</sub>O, Gly+H<sub>2</sub>O, and PD+H<sub>2</sub>O, respectively. We chose the 1:2:1 molar ratio of ChCl:principal HBD:H<sub>2</sub>O for our three DES/H<sub>2</sub>O mixtures, as Hammond *et al.* observed that at this composition for a reline/H<sub>2</sub>O mixture, water molecules contributed to the hydrogen-bonding DES network, but did not perturb



it (*i.e.* water-in-DES).<sup>9</sup> In a previous study of EG-based DES/H<sub>2</sub>O mixtures, distinct differences in the DES structure were only observed for concentrations of water greater than 30 wt.%.<sup>13</sup> The 3 DES/H<sub>2</sub>O mixtures studied here contained just ~5-6 wt.% water (Table S1, Supporting Information), which we expect leads to water-in-DES behavior for all of our formulations. It should be noted that a 1:2 molar ratio mixture of anhydrous ChCl:PD did not form a homogeneous liquid, but an opaque solid at room temperature. However, we observed that intentionally adding a small amount of water to this mixture does permit one to obtain a transparent, homogeneous solution at room temperature. While ChCl-based DESs are known to be somewhat hygroscopic, intentionally coformulating DES mixtures with a controlled amount of water can also serve to reduce the driving force for additional water vapor absorption from the ambient surroundings.

Gelatin-supported DES/mixture gels were prepared using EG+H<sub>2</sub>O, EG, PD+H<sub>2</sub>O, Gly+H<sub>2</sub>O, and Gly, all with a 20 wt.% gelatin (80 wt.% liquid) content. The resulting gels were optically transparent and freestanding, as shown in Figure 1(b). Although the gel mechanical properties are dependent upon the gelatin concentration, and our previous work demonstrated that the ultimate tensile strength can be improved by further increasing the gelatin content for EG-based DES gels,<sup>6</sup> we chose 20 wt.% gelatin in this study for processing practicality. Notably, for the Gly-based DES gels, it was difficult to repeatably obtain clear, homogeneous gel precursor solutions without included air bubbles at concentrations well above 20 wt.% gelatin, as the precursor solution becomes extremely viscous.



**Figure 2.** Room temperature ionic conductivity values of the five DES/mixture liquid formulations (unfilled bars) and their corresponding 20 wt.% gelatin-supported gel electrolyte composites (filled bars). The error bars shown represent one standard deviation among replicates ( $n \geq 3$ ) or 0.1 mS/cm, whichever was larger.

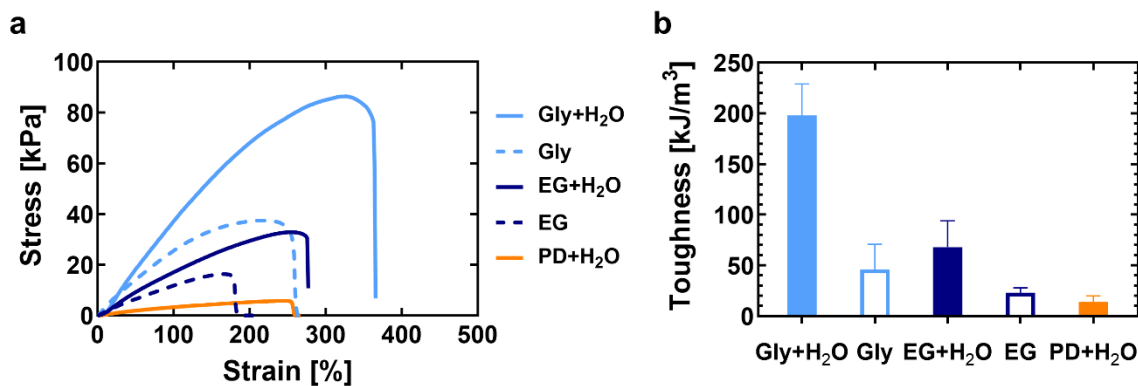
Figure 2 shows the measured room temperature ionic conductivity values of the DES/mixture liquids and their corresponding 20 wt.% gelatin gels for each of the five formulations. As expected, the liquids all displayed higher ionic conductivity than their gel counterparts, as the gelatin biopolymer scaffold impedes ionic motion and is nonconductive itself. The EG+H<sub>2</sub>O and Gly+H<sub>2</sub>O mixtures also displayed higher ionic conductivities compared to their nonaqueous versions, which is due to the reduced viscosity of the water/DES mixtures that boosts ionic mobility. The EG-based gel formulations yielded the highest ionic conductivity values:  $5.2 \pm 0.1$  mS/cm and  $3.3 \pm 0.1$  mS/cm for the EG+H<sub>2</sub>O and EG gels, respectively. The Gly gel was the least conductive of the five, at  $0.9 \pm 0.1$  mS/cm. Many previous studies have demonstrated an inverse relationship between gel electrolyte stiffness and ionic conductivity; however, while the

PD+H<sub>2</sub>O gel possessed the lowest stiffness among the formulations studied here (*vide infra*), interestingly, it was not the one that showed the highest ionic conductivity.

**Table 1.** Measured liquid densities and their comparison with literature values.

| Liquid               | Density (this work)  | Density (reported <sup>ref</sup> ) |
|----------------------|----------------------|------------------------------------|
|                      | [g/cm <sup>3</sup> ] | [g/cm <sup>3</sup> ]               |
| Gly+H <sub>2</sub> O | 1.13                 | -                                  |
| Gly                  | 1.18                 | 1.18 <sup>15</sup>                 |
| EG+H <sub>2</sub> O  | 1.12                 | -                                  |
| EG                   | 1.12                 | 1.12 <sup>15</sup>                 |
| PD+H <sub>2</sub> O  | 1.08                 | -                                  |

Table 1 presents the measured liquid densities of the five formulations studied here and compares them with values previously reported in the literature, if available. The PD+H<sub>2</sub>O liquid possessed the lowest density at 1.08 g/cm<sup>3</sup>, and Gly (DES) the highest, at 1.18 g/cm<sup>3</sup>. The density data reveals that the relative changes in the EG versus Gly DES densities due to the incorporation of 25 mol% water are different. There is a larger decrease in density observed for the Gly+H<sub>2</sub>O liquid compared to the anhydrous Gly DES (1.13 vs. 1.18 g/cm<sup>3</sup>) that is not reflected in the EG+H<sub>2</sub>O and EG systems (unchanged density of 1.12 g/cm<sup>3</sup>). Future experimental and computational studies will be helpful to probe DES/H<sub>2</sub>O mixture density trends over a broader range of water concentrations.



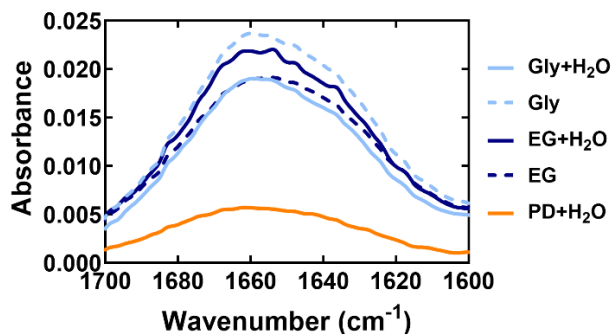
**Figure 3.** (a) Representative tensile stress-strain curves for the investigated DES/mixture gels (each contains 20 wt.% gelatin). (b) Average toughness values of the DES/mixture gels. Error bars represent one standard deviation among replicates ( $n \geq 3$ ).

Tensile tests were performed in order to evaluate gel mechanical properties (see Figure S2, Supporting Information), and representative stress-strain data are shown in Figure 3(a). From these data, gel Young's modulus, strain at break, and toughness values were extracted (Table 2). The results from the tensile tests demonstrate that there are clear variations in 20 wt.% gelatin-supported gel stiffness values, which depend on the principal (organic) HBD within the DES. Gly-based gels exhibited greater Young's moduli than EG-based gels, while the PD+H<sub>2</sub>O gel exhibited the lowest modulus of all samples at  $7 \pm 2$  kPa. These results indicate that HBD selection has a large effect on DES/H<sub>2</sub>O gel mechanical properties, which suggests that the HBD may greatly impact how gelatin self-assembles upon cooling *in situ* within the DES/H<sub>2</sub>O mixture environment. Therefore, HBD identity is a second parameter, besides polymer content, that can be used to tune the mechanical properties of these gel electrolytes. This could have great implications for designing ionic skins that more closely resemble the resiliency of the underlying tissues that they intend to mimic or interface with.

**Table 2.** Mechanical properties extracted from tensile test data for the investigated DES/mixture gels (each contains 20 wt.% gelatin). Error represents one standard deviation among replicates ( $n \geq 3$ ).

| <b>Gel Formulation</b> | <b>Modulus (kPa)</b> | <b>Strain at Break (%)</b> | <b>Toughness (kJ/m<sup>3</sup>)</b> |
|------------------------|----------------------|----------------------------|-------------------------------------|
| Gly+H <sub>2</sub> O   | 42 ± 8               | 374 ± 31                   | 198 ± 31                            |
| Gly                    | 32 ± 11              | 193 ± 58                   | 46 ± 25                             |
| EG+H <sub>2</sub> O    | 26 ± 6               | 270 ± 64                   | 68 ± 26                             |
| EG                     | 15 ± 1               | 190 ± 17                   | 23 ± 5                              |
| PD+H <sub>2</sub> O    | 7 ± 2                | 270 ± 59                   | 14 ± 6                              |

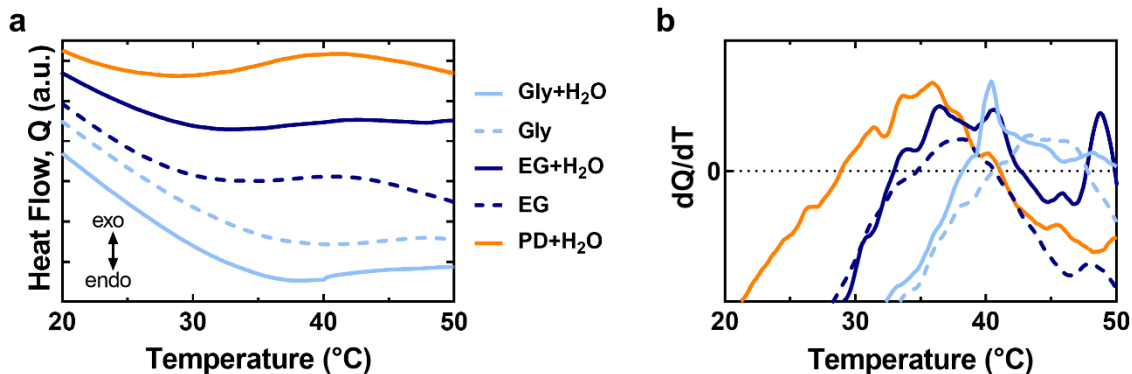
Another major finding from the tensile testing data is the impact that the intentional addition of water has on the resulting DES/mixture gel mechanical properties. While gelatin-supported hydrogels formed in deionized water alone exhibit both low stiffness and a brittle character,<sup>6</sup> the coformulation of 25 mol% water in both the Gly and EG DESs results in gelatin-supported DES/H<sub>2</sub>O mixture gels that possess even higher stiffnesses and improved stretchability compared to their nonaqueous DES gel counterparts. Toughness values of both the EG+H<sub>2</sub>O and Gly+H<sub>2</sub>O gels were found to increase substantially, approximately three- to four-fold, compared to those of the nonaqueous EG and Gly gels, respectively (see Figure 3(b) and Table 2).



**Figure 4.** FTIR spectra of 20 wt.% gelatin-supported DES/mixture gels spanning the 1600-1700  $\text{cm}^{-1}$  wavenumber region that corresponds to the amide I band inherent to gelatin (background spectra from each liquid formulation have been subtracted).

Figure 4 displays the FTIR absorbance spectra of the five DES/mixture gel formulations with the corresponding liquid absorption spectra subtracted out as a background signal. Due to the strong IR absorbance of water around 1640  $\text{cm}^{-1}$ ,<sup>16</sup> each liquid spectrum was subtracted in order to elucidate the IR absorbance contributions from the gelatin polymeric scaffold itself, which is particularly important for the three HBD+H<sub>2</sub>O formulations. The raw FTIR spectra of the gels and their neat liquids are provided in Figures S2(a) and S2(b), respectively. The wavenumber region shown in Figure 4, 1600-1700  $\text{cm}^{-1}$ , is a common range of interest for examining the amide I band, which reveals information regarding the secondary structure of polypeptides, including gelatin.<sup>17,18</sup> The broad absorbance signals within this band have previously been attributed to both gelatin triple helices (peak located at a higher wavenumber within this range,  $\sim 1660 \text{ cm}^{-1}$  here) and to nonhelical gelatin strands (peak located at a lower wavenumber within this range,  $\sim 1640 \text{ cm}^{-1}$  here).<sup>16,19</sup> The spectra shown in Figure 4 therefore indicate that gelatin triple helices do indeed form within both DES and DES/H<sub>2</sub>O mixture systems, as this is the

dominant peak observed in the spectra. Furthermore, the spectra for all gel samples are broad, indicating the coexistence of both triple helix and random coil formations of gelatin within them.



**Figure 5.** (a) DSC data obtained upon heating for the DES/mixture gel formulations; curves have been vertically offset for clarity. (b) First derivatives of the DSC traces shown in panel (a).

To further interrogate differences in the relative gelatin triple helix concentration and helical junction length among the formulations, we performed DSC measurements on the five DES/mixture gels. Figure 5(a) shows the DSC traces obtained upon heating, while Figure 5(b) shows the first derivative of each trace for easier identification of the melting temperature ( $T_m$ ) as the location of the first derivative sign change (from negative to positive). The DSC data show a shift in the DES/H<sub>2</sub>O mixture gel  $T_m$  values to higher temperatures as the principal HBD identity changes from PD to EG to Gly, in a trend that mirrors the one seen in the gel mechanical property data summarized in Table 2. The softest, least tough gel (PD+H<sub>2</sub>O) exhibits a  $T_m$  that is approximately 9  $^{\circ}\text{C}$  lower compared to that of the stiffest, toughest gel (Gly+H<sub>2</sub>O): 29  $^{\circ}\text{C}$  versus 38  $^{\circ}\text{C}$ , respectively.

Previous studies have shown that there exists no sharp boundary for the gelatin helix-coil transition,<sup>20</sup> and that  $T_m$  in gelatin hydrogels is generally viewed as corresponding to the

breaking of hydrogen bonds between gelatin chains that form triple helices. Thus, a higher  $T_m$  corresponds to a greater thermal stability of the helices. Gornall and Terentjev found that the total helix content required to gel pure EG organogels (not EG DES gels) is reduced versus their hydrogel analogues.<sup>21</sup> They attributed this to the formation of shorter triple helices that self-assemble in the EG solvent, providing a higher crosslink density for a fixed gelatin content. Thus, the minimum stable helix length to achieve gelation was suggested to be reduced for a higher observed gel  $T_m$ .<sup>21</sup> Guo and coworkers investigated critical nucleus structures involved in the self-assembly of triple helices.<sup>22</sup> They proposed two structures, a looped triple helix, whereby a chain had multiple segments taking part in the helix formation (thus the triple helix is not made up of three distinct chains, but rather one or two chains that have looped back on themselves), and a non-looped triple helix, whereby three different chains interact to form the triple helix. The authors found that the minimum stable helix length for a non-looped helix was smaller versus a looped helix.<sup>22</sup> With this in mind, our results from Figure 5 suggest that EG- and Gly-based DES/mixture gels may facilitate the formation of shorter, non-looped triple helices, with Gly-based gels exhibiting the shortest average helix length overall. On the molecular level, this may be explained by the larger size of Gly or EG versus H<sub>2</sub>O, as the principal HBD could sterically hinder the looping of gelatin chains back upon themselves.

This proposed model corresponds well with the gel mechanical properties summarized in Figure 3. For the same fixed concentration of gelatin, shorter average triple helices would allow for a greater density of helical crosslinks per volume. Thus, DES/mixtures that facilitate the formation of shorter triple helices would exhibit higher gel stiffnesses, as they contain more effective crosslinks within the polymer network. However, we observed that the  $T_m$  values of the nonaqueous Gly and EG DES gels were slightly larger ( $\sim 2$  °C) than their DES/H<sub>2</sub>O mixture gel



counterparts. Water may help to facilitate nonhelical interchain hydrogen bonding,<sup>21,23</sup> thus potentially creating a greater number of dynamic crosslinks within the scaffold. It may also preferentially interact with/hydrate chloride ions within the system,<sup>24</sup> promoting the formation of more gelatin interchain aggregates. Either of these could explain why the stretchability (maximum strain at break) of the HBD+H<sub>2</sub>O gels was observed to be substantially larger compared to their nonaqueous analogues (Figure 3). Our present findings collectively suggest that the controlled amount of intentional water added in the HBD+H<sub>2</sub>O systems (*i.e.* 25 mol% or ~5-6 wt.% of the liquid mixture) does not behave as bulk water, consistent with the conclusions of several previous computational studies,<sup>9,12,13</sup> but instead participates mainly in hydrogen bonding with the DES components and the gelatin biopolymer. There is an inherent intermolecular competition between many different potential hydrogen bonding partners in these systems that the field is still just beginning to understand. In a future study, we plan to more directly probe the structural details of the gelatin scaffold within these DES/mixture gels using radiation scattering techniques, and to investigate the hydrated DES gel molecular environment via molecular dynamics simulations.

## CONCLUSIONS

This work has explored how the organic HBD identity and/or the presence of a controlled amount of water (5-6 wt.%) can influence the self-assembly of gelatin *in situ* within DES/mixture gel electrolytes to tune their mechanical properties and ionic conductivities. We observed an approximately 9 °C temperature difference in thermal stability between that of the softest gel (7 kPa modulus, PD+H<sub>2</sub>O gel) and that of the stiffest gel (42 kPa modulus, Gly+H<sub>2</sub>O gel). We propose that the organic HBD may influence the average length of gelatin triple helices

that assemble in such systems, and that gels containing the shortest average helices can exhibit the largest stiffnesses, as they may possess a greater density of helices for a fixed total polymer content. All five of the gelatin-supported DES/mixture gel formulations tested here exhibited tensile strain at break values of nearly 200% strain or larger. Notably, the addition of water to the DES/mixture systems was found to improve the toughness of their resulting gelatin-supported gels. The tensile toughness of 20 wt.% gelatin gels based on the well-studied DES 1:2 ChCl:EG could be increased from 23 to 68 kJ/m<sup>3</sup> by coformulating this DES with 25 mol% water, and the increase for Gly-based gels was even larger (46 to 198 kJ/m<sup>3</sup>). We believe that this could be due to water-chloride interactions that facilitate the formation of additional dynamic crosslinks between polymer chains. The presence of water is also observed to increase the ionic conductivity of both the DES/water mixtures and their corresponding gelatin-supported gels alike, in comparison to nonaqueous DES analogues. The results of this study can serve to inform thoughtful materials selection when designing DES gel-based ionic skins, as the choice of HBD(s) can greatly influence the ultimate mechanical and ionic transport properties of this emerging class of ion-dense gel electrolytes.

## ASSOCIATED CONTENT

### **Supporting Information**

DES/mixture liquid compositions, gel tensile testing photographs, and raw FTIR spectra (PDF).

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## Notes

The authors declare no competing financial interest.

## Acknowledgement

This work was partially supported by the NSF through an IGERT grant (DGE-1144591), by NSF CBET-1935555, and by Tufts University.

## REFERENCES

- (1) Sun, J. Y.; Keplinger, C.; Whitesides, G. M.; Suo, Z. Ionic Skin. *Adv. Mater.* **2014**, *26*, 7608–7614. <https://doi.org/10.1002/adma.201403441>.
- (2) Keplinger, C.; Sun, J. Y.; Foo, C. C.; Rothmund, P.; Whitesides, G. M.; Suo, Z. Stretchable, Transparent, Ionic Conductors. *Science* **2013**, *341*, 984–987. <https://doi.org/10.1126/science.1240228>.
- (3) Cao, Y.; Tan, Y. J.; Li, S.; Lee, W. W.; Guo, H.; Cai, Y.; Wang, C.; Tee, B. C.-K. Self-Healing Electronic Skins for Aquatic Environments. *Nat. Electron.* **2019**, *2*, 75–82. <https://doi.org/10.1038/s41928-019-0206-5>.
- (4) Zhang, L. M.; He, Y.; Cheng, S.; Sheng, H.; Dai, K.; Zheng, W. J.; Wang, M. X.; Chen, Z. S.; Chen, Y. M.; Suo, Z. Self-Healing, Adhesive, and Highly Stretchable Ionogel as a Strain Sensor for Extremely Large Deformation. *Small* **2019**, 1804651. <https://doi.org/10.1002/sml.201804651>.

- (5) Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* **2014**, *114*, 11060–11082. <https://doi.org/10.1021/cr300162p>.
- (6) Qin, H.; Owyung, R. E.; Sonkusale, S. R.; Panzer, M. J. Highly Stretchable and Nonvolatile Gelatin-Supported Deep Eutectic Solvent Gel Electrolyte-Based Ionic Skins for Strain and Pressure Sensing. *J. Mater. Chem. C* **2019**, *7*, 601–608. <https://doi.org/10.1039/c8tc05918g>.
- (7) Qin, H.; Panzer, M. J. Chemically Cross-Linked Poly(2-Hydroxyethyl Methacrylate)-Supported Deep Eutectic Solvent Gel Electrolytes for Eco-Friendly Supercapacitors. *ChemElectroChem* **2017**, *4*, 2556–2562. <https://doi.org/10.1002/celc.201700586>.
- (8) Lopez-Salas, N.; Vicent-Luna, J. M.; Imberti, S.; Posada, E.; Roldan, M. J.; Anta, J. A.; Balestra, S. R. G.; Castro, R. M. M.; Calero, S.; Jimenez-Rioboo, R. J.; Gutierrez, M. C.; Ferrer, M. L.; del Monte, F. Looking at the “Water-in-Deep-Eutectic-Solvent ” System: A Dilution Range for High Performance Eutectics. *ACS Sustainable Chem. Eng.* **2019**, *7*, 17565-17573. <https://doi.org/10.1021/acssuschemeng.9b05096>.
- (9) Hammond, O. S.; Bowron, D. T.; Edler, K. J. The Effect of Water upon Deep Eutectic Solvent Nanostructure: An Unusual Transition from Ionic Mixture to Aqueous Solution. *Angew. Chemie Int. Ed.* **2017**, *56*, 9782–9785. <https://doi.org/10.1002/anie.201702486>.
- (10) Fetisov, E. O.; Harwood, D. B.; Kuo, I. F. W.; Warrag, S. E. E.; Kroon, M. C.; Peters, C. J.; Siepmann, J. I. First-Principles Molecular Dynamics Study of a Deep Eutectic Solvent: Choline Chloride/Urea and Its Mixture with Water. *J. Phys. Chem. B* **2018**, *122*, 1245–1254. <https://doi.org/10.1021/acs.jpcb.7b10422>.
- (11) Dai, Y.; Witkamp, G. J.; Verpoorte, R.; Choi, Y. H. Tailoring Properties of Natural Deep

- Eutectic Solvents with Water to Facilitate Their Applications. *Food Chem.* **2015**, *187*, 14–19. <https://doi.org/10.1016/j.foodchem.2015.03.123>.
- (12) Zhekenov, T.; Toksanbayev, N.; Kazakbayeva, Z.; Shah, D.; Mjalli, F. S. Formation of Type III Deep Eutectic Solvents and Effect of Water on Their Intermolecular Interactions. *Fluid Phase Equilib.* **2017**, *441*, 43–48. <https://doi.org/10.1016/j.fluid.2017.01.022>.
- (13) Jani, A.; Sohier, T.; Morineau, D. Phase Behavior of Aqueous Solutions of Ethaline Deep Eutectic Solvent. *J. Mol. Liq.* **2020**, 112701. <https://doi.org/10.1016/j.molliq.2020.112701>.
- (14) D’Agostino, C.; Gladden, L. F.; Mantle, M. D.; Abbott, A. P.; Ahmed, E. I.; Al-Murshedi, A. Y. M.; Harris, R. C. Molecular and Ionic Diffusion in Aqueous-Deep Eutectic Solvent Mixtures: Probing Inter-Molecular Interactions Using PFG NMR. *Phys. Chem. Chem. Phys.* **2015**, *17*, 15297–15304. <https://doi.org/10.1039/c5cp01493j>.
- (15) Abbott, A. P.; Harris, R. C.; Ryder, K. S. Application of Hole Theory to Define Ionic Liquids by Their Transport Properties. *J. Phys. Chem. B* **2007**, *111*, 4910–4913. <https://doi.org/10.1021/jp0671998>.
- (16) Polyak, F.; Reich, G. Infrared Spectroscopic Study of the Coil-Helix Transition of Highly Concentrated Gelatin Formulations. *Eur. J. Pharm. Biopharm.* **2019**, *140*, 11–19. <https://doi.org/10.1016/j.ejpb.2019.04.010>.
- (17) Fabian, H.; Mantele, W. Infrared Spectroscopy of Proteins. In *Handbook of Vibrational Spectroscopy*; Chalmers, J. M., Ed.; John Wiley & Sons, Ltd: Chichester, UK, 2006. <https://doi.org/10.1002/0470027320.s8201>.
- (18) Barth, A. Infrared Spectroscopy of Proteins. *Biochimica et Biophysica Acta* –

- Bioenergetics* **2007**, 1767, 1073–1101. <https://doi.org/10.1016/j.bbabbio.2007.06.004>.
- (19) Prystupa, D. A.; Donald, A. M. Infrared Study of Gelatin Conformations in the Gel and Sol States. *Polym. Gels Networks* **1996**, 4, 87–110. [https://doi.org/10.1016/0966-7822\(96\)00003-2](https://doi.org/10.1016/0966-7822(96)00003-2).
- (20) Gornall, J. L.; Terentjev, E. M. Concentration-Temperature Superposition of Helix Folding Rates in Gelatin. *Phys. Rev. Lett.* **2007**, 99, 028304. <https://doi.org/10.1103/PhysRevLett.99.028304>.
- (21) Gornall, J. L.; Terentjev, E. M. Helix-Coil Transition of Gelatin: Helical Morphology and Stability. *Soft Matter* **2008**, 4, 544–549. <https://doi.org/10.1039/b713075a>.
- (22) Guo, L.; Colby, R. H.; Lusignan, C. P.; Whitesides, T. H. Kinetics of Triple Helix Formation in Semidilute Gelatin Solutions. *Macromolecules* **2003**, 36, 9999–10008. <https://doi.org/10.1021/ma034264s>.
- (23) Duconseille, A.; Gaillard, C.; Santé-Lhoutellier, V.; Astruc, T. Molecular and Structural Changes in Gelatin Evidenced by Raman Microspectroscopy. *Food Hydrocoll.* **2018**, 77, 777–786. <https://doi.org/10.1016/j.foodhyd.2017.11.020>.
- (24) Sapir, L.; Harries, D. Restructuring a Deep Eutectic Solvent by Water: The Nanostructure of Hydrated Choline Chloride/Urea. *J. Chem. Theory Comput* **2020**, 6, 2020, *in press*. <https://doi.org/10.1021/acs.jctc.0c00120>.

## TOC Graphic

