Self-Assembled Gels formed in Deep Eutectic Solvents – Supramolecular Eutectogels with High Ionic Conductivities

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Abstract: This paper reports the ability of 1,3:2,4-dibenzylidene-D-sorbitol (DBS), a simple, commercially-relevant compound, to self-assemble as a result of intermolecular non-covalent interactions into supramolecular gels in deep eutectic solvents (DESs). The DESs are based on choline chloride combined with alcohols/ureas – DBS forms gels at a loading of 5% wt/vol. Rheology confirms the gel-like nature of the materials, electron microscopy and X-ray diffraction indicate underpinning nanofibrillar DBS networks and differential scanning calorimetry shows the deep eutectic solvent nature of the liquid-like phase is retained. The ionic conductivities of the gels are similar to those of the unmodified DESs proving the deep eutectic nature of the ionic liquid-like phase. Gelation is tolerant of ionic additives Li+, Mg2+ and Ca2+, with the resulting gels having similar conductivities to electrolyte dissolved in the native DES. The low-molecular-weight gelator DBS is a low-cost additive – forming gels in DESs from readily-available constituents, with conductivity levels suitable for practical applications. We suggest supramolecular eutectogels have potential uses ranging from energy technology to synthesis and catalysis.

Deep eutectic solvents (DESs) are a specific class of ionic liquid first developed by Abbott and co-workers.[1] In contrast to traditional ionic liquids (ILs), which are composed of a discrete anion and cation,[2] DESs are typically formed by mixing a quaternary ammonium salt with a hydrogen bond donor (or metal salt).[3] The hydrogen bond donor interacts with the anion to generate a larger non-symmetrical ion, hence decreasing the melting point – in this way, two components that individually are solids can mix to form a liquid-like phase. DESs are a fascinating example in which hydrogen-bond-mediated anion binding, a key theme in supramolecular chemistry,[4] leads to significant changes in bulk materials properties. Like traditional ionic liquids, many DESs have low vapour pressure, low-flammability and wide liquid range, but also have additional advantages, including ease of preparation and the use of relatively inexpensive, non-toxic components. These solvents are being extensively explored for a wide range of uses, including metal processing,[5] organic synthesis/catalysis,[6] nanomaterials synthesis,[7] analytical chemistry,[8] biotechnology,[9] and energy applications.[10]

There has previously been considerable interest in structuring traditional ILs into soft materials such as gels – generating 'ionogels'.[11] Gels are well-known colloidal soft materials in which a 'solid-like' network extends through a 'liquid-like' phase leading

to sample immobilisation. The solid-like network in gels is most commonly crosslinked or entangled polymers,[12] but can also be composed of small molecules (low-molecular-weight gelators, LMWGs) that self-assemble into a nanoscale network as a result of intermolecular non-covalent interactions.[13] In 2001, landmark research from Kimizuka and Nakashima reported glycolipid LMWGs that assembled into bilayer membranes capable of immobilising ILs.[14] Hanabusa and co-workers then reported a family of dipeptide gelators functionalised with a branched alkyl chain, which they described as specialist gelators for ILs, importantly noting that gel conductivities were similar to those of the native ILs.[15] Later work with other LMWGs in ILs also indicated that electrochemical properties of the gels were similar to those of the ILs.[16] Such materials have been incorporated as gel electrolytes into devices like solar cells.[17]

Remarkably, although there has been considerable development of ionogels based on traditional ILs, gels based on deep eutectic solvents (DESs) have seen much less attention, with relatively few reports using polymers or silicas to immobilise DESs.[18] A recent study used silica-based materials to immobilise DESs, referring to the resulting gels for the first time as 'Eutectogels', and demonstrating their application in Li/Li-ion batteries.[19] However, to the best of our knowledge, there are no reports of supramolecular gels formed in DESs via self-assembly. In some cases, two-component 'deep eutectic' systems have themselves been applied as supramolecular gelators by addition to traditional solvents[20] – but this is significantly different to developing supramolecular gelators that can be added to DESs, hence immobilising them, as targeted here. As noted above, DESs have inherent non-covalent interactions within their structures, which may interfere with self-assembly of the LMWG into a nanoscale network (or the LMWG may limit DES performance) – such processes urgently need study.

We therefore targeted supramolecular gels based on DESs, reasoning such materials could have very high value in (e.g.) energy applications. With a view towards industrial relevance, we decided to explore whether gels could be formed based on 1,3:2,4-dibenzylidene-D-sorbitol (DBS).[21] This commercially-available gelator is synthesised by condensation of naturally occurring sorbitol with two equivalents of benzaldehyde.[22] It is used in a wide-range of current applications from personal care products to polymer additives and is synthesised on bulk scale at low cost.[21] At present, although solvent effects on gelation can often be well predicted for organic solvents,[23] it is not possible to easily predict solvent effects in ILs or DESs, let alone extrapolate them to the field of gelation.[24] We were therefore unsure whether DBS would act as a gelator for DESs. However, we considered DBS a good candidate LMWG because it assembles through a combination of hydrogen bonds and solvophobic interactions, the balance of which varies depending on solvent.[25]

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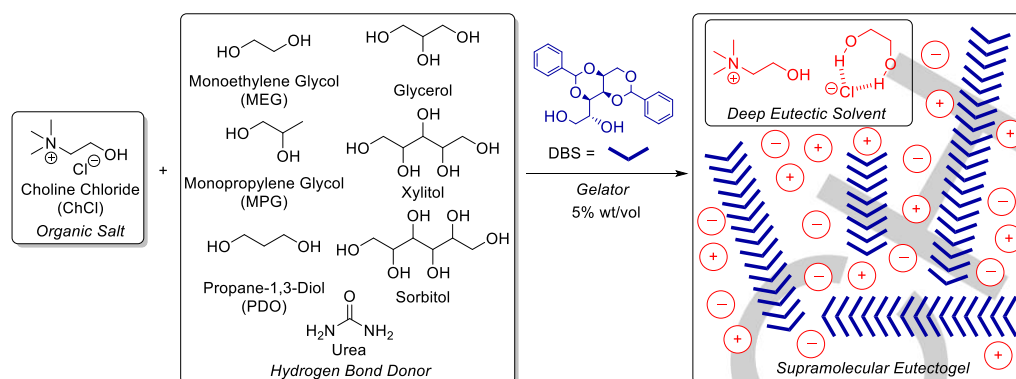   the document

Figure 1. Deep eutectic solvents formed by mixing an organic salt and a hydrogen bond donor (1:2 ratio) can turned into gel-phase materials by the addition of 1,3:2,4-dibenzylidene-D-sorbitol (DBS, 5% wt/vol), which self-assembles into nanofibres, forming a new class of '*supramolecular eutectogels*'.

In preliminary work, we found DBS was an effective gelator of glycols such as 1,2-ethyleneglycol, in the presence of polar additives like water. Given DESs are based on such alcohols combined with ionic salts, we reasoned there was scope for this gelator to adapt to the DES environment and self-assemble.

We initially focussed attention on DESs based on choline chloride (ChCl) combined with a small family of hydrogen bond donors (monoethylene glycol, MEG; monopropylene glycol, MPG; 1,3-propane-diol, PDO) in a 1:2 molar ratio (Fig. 1). We tested these DESs to determine whether DBS formed gels. Gelator loadings of 3% wt/vol were used first, but gelation did not occur, with turbid solutions mostly being obtained. Usually, DBS forms gels in such solvents at loadings <1%, so it seems likely that ionic ChCl suppresses gelation. This is not surprising as the chloride anion, present at high concentration in the DES, can potentially interact with the hydroxyl groups on DBS,[26] which may hinder DBS from establishing its own self-assembled network. Pleasingly, however, on raising DBS loading further, gels formed after a heat/cool cycle (to dissolve the DBS) at loadings ≥ 4% wt/vol in ChCl:MEG (1:2) (Fig. S2). Gelation was also readily triggered by ultrasound, cutting gelation time to ca. 10 s, compared with ca. 1 h in ambient heat/cool conditions. Gels were fully transparent in MEG, and just slightly cloudy in MPG or PDO suggesting we are not simply observing 'gel-like' materials due to DBS insolubility, but achieving a well-dispersed nanoscale network (see below). We thus refer to these innovative materials as *supramolecular eutectogels*. We also probed the ability to form gels in DESs based on different ChCl:MEG ratios. Effective gels also formed in 1:3 and 1:4 ratios (Figs. S10, S11). A 1:1 ChCl:MEG ratio did not form a liquid at room temperature.

Thermal stabilities for the 1:2 DESs were determined using reproducible tube inversion methodology. The T_{gel} value (gel-sol transition onset temperature) was highest for MEG (84°C) > PDO (79°C) > MPG (76°C) – suggesting more thermally stable gels form in the more polar MEG-based DES. This matches the observation that the MEG gel was most transparent, suggesting the best compatibility between DBS and DES. It is well-known that solvent parameters influence the performance of supramolecular gels,[23] and it would appear this is also true in DESs. We also probed the dependence of T_{gel} on the

concentration of DBS (Fig. S3) and found the normally observed relationship for supramolecular gels in which the T_{gel} value increases with loading from 82°C at 4% wt/vol to 111°C at 10% wt/vol, as expected based on DBS establishing a more effective sample-spanning network. Furthermore, the T_{gel} value was essentially invariant with the precise composition of the DES, across ChCl:MEG ratios ranging from 1:1.5 to 1:2.5 (Figs. S8, S9).

With these gels in hand, we went on to expand the range of H-bond donors that could be incorporated into the DES, specifically targeting systems that could be made from renewable natural resources[27] – in this way, both DES and the DBS gelator would be constructed from naturally-occurring starting materials. We tested DESs based on ChCl combined with glycerol, xylitol, sorbitol and urea, in a 1:2 ratio (Fig. 1). In each case, addition of DBS (5% wt/vol) gave rise to gels. In particular, we probed the ChCl:urea (1:2) and ChCl:glycerol (1:2) systems in more detail (Figs. S4-S7) – determining the effect of DBS concentration on gel thermal stability – these systems once again behaved like normal supramolecular gel-phase materials, with T_{gel} values being tuned between 110°C and 140°C.

To further investigate macroscopic performance, rheological characterisation of these supramolecular eutectogels was performed on samples made as discs. These gels are hygroscopic and samples were thus made in a closed vial with a removable base, transferred to the rheometer and tested (Fig. S1). The gels can be relatively easily handled, unusual for supramolecular gels, many of which are soft and readily damaged. The high loading of DBS will clearly help, but nonetheless, these eutectogels are relatively robust. In each case, the materials were gels, with G' (elastic modulus) larger than G'' (viscous modulus) (Figs. S12-S20). The G' values were large at ca. 5×10^5 - 2×10^6 Pa indicating stiff gels. Gels broke down when the shear strain was ca. 0.5%. For gels based on MEG, PDO and MPG, the stiffness increased from MEG to PDO to MPG (Fig. S15), suggesting that as the compatibility of solvent for DBS decreases (see above), the gel becomes stiffer. Overall, however, in rheological terms these gels were all fairly similar.

To characterise these gels at the nanoscale using electron microscopy, sample preparation is vital. For gels, some sort of drying step is required, but the presence of low volatility

components such as choline chloride in DESs is problematic, as they will simply crystallise/precipitate. We therefore used a solvent exchange method, placing a piece of gel in water for 3 days, with the water being replaced every 24 hours. This exchanges the DES with water. We cannot rule out that the gel scaffold may reorganise somewhat during solvent exchange, but the macroscopic stability of the gel during this process indicates its underpinning network structure is maintained.[28] Samples that had been solvent exchanged with water were then cryo-dried at liquid nitrogen temperature under high vacuum, limiting network reorganisation. Scanning electron microscopy (SEM, Fig. 2 and Figs. S24-S26) clearly indicated the presence of nanofibres, which were visually equivalent in each case with diameters of 20-50 nm. These were similar in morphology to previous reports of DBS in polyethyleneglycol.[29] Transmission electron microscopy (TEM, Fig. 2 and Figs. S30-S36) also indicated self-assembled nanofibres. Imaging and rheology therefore support the view that DBS self-assembles into supramolecular gels in these DESs.
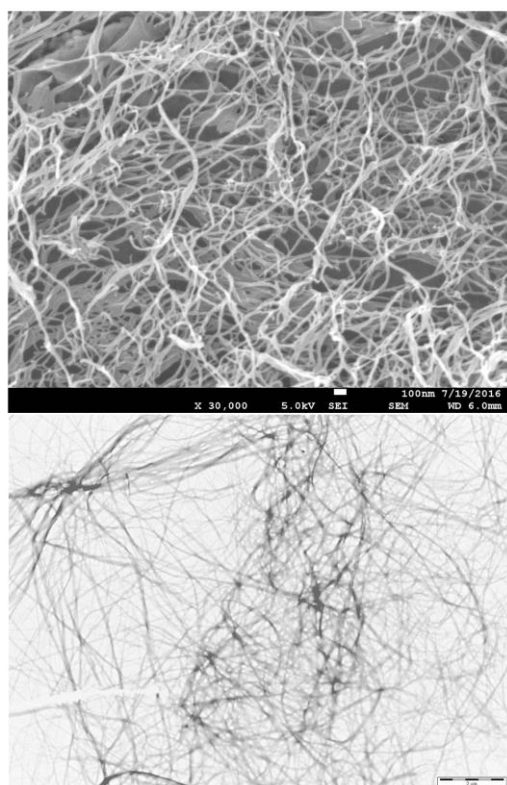

Fig. 2. SEM (top, scale bar = 100 nm) and TEM (bottom, scale bar = 2 μm) images of supramolecular eutectogel made in ChCl:MEG, then solvent exchanged with water and cryo-dried prior to imaging.

To gain further insight into the molecular packing within these gel fibres we performed XRD analysis on dried samples of the gels (Figs S50-S53). However, it was not possible to effectively dry the gels directly from the deep eutectic state and a broad peak was observed reflecting the disordered nature of the system (Fig. S50). If the gel was solvent exchanged with water and then dried, some small peaks at smaller angles associated with fine structure were observed (Fig. S52). Importantly, these peaks were in agreement with the much larger X-ray peaks observed from a fully

dried DBS gel formed in EtOH/H$_2$O (1:1) – we therefore suggest that the small fine structure peaks observed in the DES gel are consistent with self-assembled DBS having a similar packing arrangement to conventional gels. In-line with the literature, we did not assign the XRD, but note that the 'fingerprint' is similar to that reported by others for gels based on DBS.[30]

To ensure the deep eutectic nature of the liquid-like phase of the gels, we performed differential scanning calorimetry (DSC) over a temperature range of -70°C to 90°C (Figs. S40-S49). For the native DESs, we typically observed endotherms associated with solid-liquid transitions on heating from -70°C, as in the literature.[31] On cooling, no exotherms were observed, in agreement with reports that on cooling below the melting point, DESs form supercooled liquids.[32] In the presence of the DBS gelator (5% wt/vol), very similar DSC traces were obtained. The peaks associated with DES melting were somewhat broader than for the native DESs, suggesting slightly less cooperative transitions in the presence of a gel network, but supporting the view that the liquid-like phase of these gels retains its DES nature.
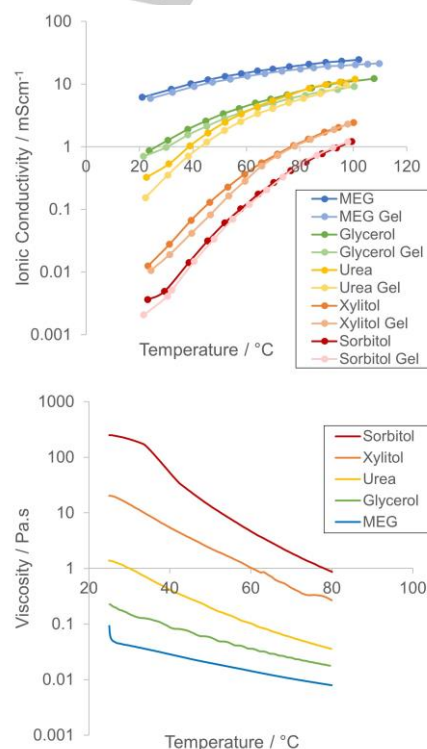

Figure 3. Top: Ionic conductivity of different DESs (darker colours) and eutectogels (lighter gels) based on ChCl:Hydrogen Bond Donor (1:2) with DBS (5% wt/vol), plotted against temperature – conductivity is maintained with the self-assembled gels. Bottom: Viscosity of DESs versus temperature demonstrating that on heating, as conductivity increases, viscosity decreases.

Given many DES applications are based on conductivity,[10] we investigated the ionic conductivities (ICs) of these systems at a range of temperatures using an ionic conductometer. Initially we probed the ICs of the native DESs (Fig. 3, top, darker colours), with ICs under ambient conditions varying widely from ca. 0.001 up to 10 mS/cm, in spite of them all containing the same amount of choline chloride. This behaviour is related to the relative

viscosity of each DES.[33] Indeed, measuring viscosity (Fig. 3, bottom) indicated that the most viscous DES was based on sorbitol and the least viscous on MEG. It is clear that conductivity increases as viscosity decreases. Considering further the effect of temperature on conductivity,[34] the increase in conductivity on heating is a result of two effects: (i) lower viscosity (see above) and (ii) increased ionic mobility, at higher temperatures.

We then tested the ICs of the supramolecular eutectogels (Fig. 3, top, lighter colours). Pleasingly, these materials show very similar ICs to native DESs (Fig, 3, top, darker colours). This indicates that the presence of a self-assembled 'solid-like' nanoscale network does not significantly inhibit ion transport, which clearly still takes place in the mobile 'liquid-like' phase. It is evident that the gels formed in these DESs retain the liquid-like deep eutectic characteristics of the solvent phase, even in the presence of the self-assembled nanofibres – in agreement with DSC data described above. In general, the ICs of the gels are only very slightly lower than native DESs – similar effects are often observed in ionic liquid gels.[16] Conductivities thus correlate simply with the performance of the native DES, with the gel based on sorbitol being least conductive and that based on MEG being most conductive. Given conductivities ≥ 1mScm⁻¹ are of practical use, eutectogels based on ChCl combined with MEG (and MPG or PDO – see Fig. S59) all had useful conductivities under ambient conditions, suggesting genuine potential as gel electrolytes.[35] Of the renewable replacements for MEG, glycerol was most effective at ambient temperatures, while urea became effective on gentle heating (the melting point of ChCl:Urea is close to room temperature – Figs. S44,S45). Xylitol and sorbitol based systems were not very effective conductors – this relates to the viscosity of the liquid-like phase, rather than any inherent problem caused by the gel. Future work would aim to understand ionic diffusion in these materials in a more quantitative way.[36]
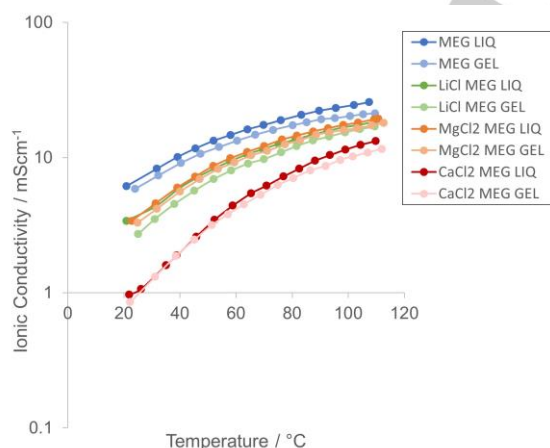

Fig. 4. Conductivity of native DES's based on ChCl/MEG and eutectogels formed in this DES with 5% wt/vol DBS, in the absence and presence of ionic additives (1 M).

Given the interest in using DES's as electrolytes, in which a variety of other ionic species can also be present,[37] we probed the impact of ionic additives on our most conductive eutectogel (DBS in ChCl:MEG). Adding salts may change the interactions between DBS molecules or between DBS and the liquid-like phase, hence affecting gelation and potentially ionic conductivity. We tested various metal chlorides as additives at concentrations from 0.05 M to 6 M. Initially, we determined their solubility in the native DES (Table S1, Figs. S54-S58). The most soluble was lithium chloride (up to 7 M) followed by iron chloride (up to 1 M), both of which gave transparent solutions. Magnesium and calcium chlorides were soluble (up to 1 M) but caused loss of liquid-like DES properties. Sodium, potassium and aluminium chlorides were largely insoluble. Gelation was tested with 1 M concentrations of the more soluble salts using DBS and a heat/cool cycle. The system containing Li⁺ formed gels, as did those containing Mg²⁺ and Ca²⁺. However, the system containing Fe³⁺ did not form a gel. We suggest that the strong Lewis acid nature of FeCl₃ hinders interactions between DBS molecules.

We investigated the impact of ionic additives on rheological performance, which given the errors in gel rheology, was relatively small – gels had similar stiffness to unmodified MEG, but broke down at slightly lower shear strain (ca. 0.2%, Figs. S21-S23). SEM and TEM imaging once again allowed us to identify nanoscale fibrillar 3D networks (Figs. S27-S29 and Figs. S37-S39, suggesting these ionic additives do not stop DBS self-assembly.

Conductivity testing in the absence of gelator (Fig. 4, darker colours) indicated that ionic salts reduced the IC to ca. 66% (Li⁺ and Mg²⁺) and ca. 33% (Ca²⁺) of the native DES. These relatively charge-dense ions lower the IC by inducing stronger ion pairing in the liquid-like phase and hence limiting ionic mobility. We then determined the ICs of the supramolecular eutectogels in the presence of these ionic additives (Fig. 4, lighter colours). In each case, gelation once again only slightly decreases conductivity. Therefore, gelation still occurs and these systems maintain conductivity – relevant with regard to electrolyte applications. We suggest this system has potential for use in Li⁺ batteries (conductivities ca. 3-4 mScm⁻¹ under ambient conditions).

In summary, DBS is an effective way of immobilising this class of deep eutectic solvents giving rise to self-assembled gels with nanofibrillar morphologies. These gels tolerate ionic salt additives such as Li⁺. Furthermore, the presence of the 'solid-like' gel network has no significant adverse effects on DES ionic conductivities. We suggest the deep eutectic liquid-like phase of the gel remains highly dynamic, allowing ionic charge propagation. Given the commercial relevance of DBS, this is a simple, low-cost, environmentally-friendly way of imparting DESs with desirable gel-phase materials properties. Ultimately, these supramolecular eutectogels have potential applications ranging from energy technology to synthesis and catalysis.

Acknowledgements

Keywords: deep eutectic • conductivity • gel • ionic liquid • self-assembly • solvent • supramolecular

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Entry for the Table of Contents

COMMUNICATION

'Supramolecular eutectogels' – 1,3:2,4-dibenzylidene-D-sorbitol self-assembles into nanofibres in deep eutectic solvents based on choline chloride and various hydrogen bond donors to give conductive gels.

Deep Eutectic Solvent

Gelator =

Supramolecular Eutectogel
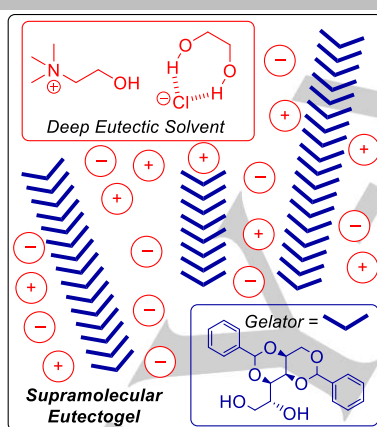
Jorge Ruiz-Olles, Nicole K. Whitelaw, David K. Smith*

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Self-Assembled Gels formed in Deep Eutectic Solvents – Supramolecular Eutectogels with High Ionic Conductivities