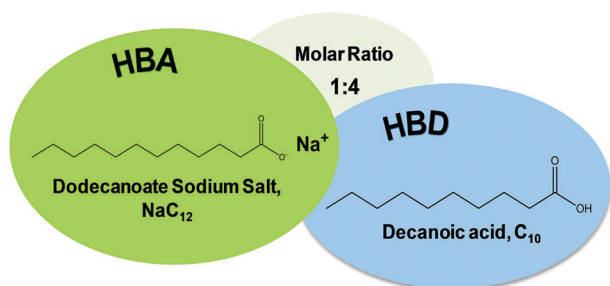


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A metallo supramolecular hydrogel based on a sodium deep eutectic solvent

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Catarina Florindo, Lucas G. Celia-Silva, Luís F. G. Martins, Luís C. Branco and Isabel M. Marrucho*

A metallo supramolecular hydrogel based on a metal containing deep eutectic solvent (DES) is presented here for the first time.

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10 **A metallo supramolecular hydrogel based on a sodium deep eutectic solvent†** 10

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20 **A metallo supramolecular hydrogel based on a metal containing deep eutectic solvent (DES) is presented here for the first time. The phase diagram of the DES-based hydrogel was drawn and its rheological properties were determined.**25 Supramolecular hydrogels or low molecular-weight gelators (LMWGs) are highly hydrated, porous materials, based on the formation of a fibrillar network by the self-assembly of molecular building blocks due to complementary non-covalent interactions, including hydrogen bonding, π - π interactions, hydrophobic interactions and metal ligand interactions.^{1,2} 30 They are typically formed through the use of ultrasound, heating or pH change, which rearranges the aggregation of molecules by cleaving self-locked intramolecular hydrogen bonds or π -stacking to form crosslinked structures through intermolecular interactions, usually involving the participation of water molecules.³ Supramolecular gels based on biocompatible compounds, for example ureas, amides, nucleobases, amino acids, surfactants, sugars, and fatty acids, among others, have been deeply investigated.¹ Recently, gelation induced by metal ions has gained huge interest due to their fascinating properties and the control over self-assembly by tuning the metal-ligand coordination. Moreover, the incorporation of different metal ions into hydrogels allows a fine control of the gel mechanical properties, through the tuning of metal-ligand interactions.⁴ Usually, supramolecular gels are 45composed of a long aliphatic chain connected with a polar head and the tendency of the head to interact in a three dimensional network enhances the probability of gel formation. Deep eutectic solvents (DESS) have been attracting a lot of attention as new sustainable solvents not only due to their favourable properties such as easy preparation with no need of further purification, good biodegradability, low toxicity, low volatility and low prices,^{5,6} but also due to their application in a wide range of fields, such as catalysis, organic synthesis, electrochemical devices, solar technology, *etc.*⁷ DESs have found an unquestionable role in extraction and separation processes, for example in the selective isolation and recovery of metals,⁸ the isolation and recovery of compounds from natural products,⁹ the desulfurization of fuels,¹⁰ azeotrope breaking,¹¹ and water purification.^{12,13}25 DESs represent a new generation of unconventional solvents which are obtained just by mixing two or more compounds, generally a salt and an amino acid,¹⁴ a carbohydrate,¹⁵ an alcohol,¹⁶ a carboxylic acid¹⁷ *etc.*, which act as a hydrogen bond acceptor (HBA) and donor (HBD), respectively. This combination of a HBA and a HBD leads to the formation of a final liquid compound, with a melting point much lower than those of the individual starting components.^{18,19} The control of the DES properties is essentially performed through the chemistry of the chosen starting compounds, but other properties such as molar ratio and water uptake, also have crucial effects.⁵ For example, most of the DESs reported are very hydrophilic and hygroscopic, due to their hydrophilic nature and the rapid establishment of a hydrogen bond network, under ambient conditions.^{20,21} Lately, the development of hydrophobic DESs has also been explored and their stability when in contact with water has been studied.^{12,22} Long chain ammonium and phosphonium salts combined with hydrophobic acids and alcohols, or even two long chain fatty acids, or natural hydrophobic compounds combined with fatty acids have been used to prepare hydrophobic DESs. In this work, we step forward and use a metal (sodium) salt derived from a long chain fatty acid (NaC₁₂) and a long chain fatty acid (C₁₀), as depicted in Fig. 1, to 50Q3 ^a Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. Da República, 2780-157, Oeiras, Portugal^b Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal50 ^c Centro de Química de Évora, Escola de Ciências e Tecnologia, Instituto de Investigação e Formação Avançada, Universidade de Évora, Rua Romão Ramalho, 59 7000-671 Évora, Portugal^d REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal

† Electronic supplementary information (ESI) available: Experimental data of characterization of the DES, namely thermal properties, density and viscosity; FTIR and DSC analysis; and rheological properties. See DOI: 10.1039/c8cc03266a 55

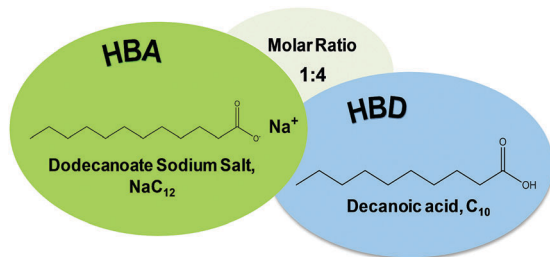


Fig. 1 Chemical structure, respective acronym and molar ratio of the new sodium salt-based DES ($\text{NaC}_{12}:\text{C}_{10}$ (1:4)) reported in this work.

prepare a DES. The use of the sodium based salt with its surfactant properties should provide DESs with different properties from those based on ammonium and phosphonium salts with long hydrocarbon chains.

The new sodium salt-based DESs may be of great interest and promise for applications, especially in medical and biotechnological fields, separations and extractions, the purification of natural products and electrochemical applications.

Abbott²³ recently reported the preparation of a family of compounds using alkali metal salts, based on sodium, potassium, magnesium and calcium salts combined with glycerol. They concluded that although none of these mixtures showed eutectic behaviour, their physical properties are similar to hydrophilic DESs.²³

In order to ascertain the eutectic behaviour of these new eutectic mixtures, the solid-liquid phase diagram was drawn, by combining several molar ratios of both components, NaC_{12} and C_{10} . The mixtures were put in a glass vial and heated at $80\text{ }^\circ\text{C}$ for DES preparation. The solid-liquid phase diagram was mapped using a visual method, where mixtures of known concentrations are heated up until only a liquid phase is observed, and is shown in Fig. ESI1 in the ESI.† Contrary to what was observed by Abbott's group, in the present case a eutectic point at a 0.80 mole fraction of C_{10} was obtained, meaning that the $\text{NaC}_{12}:\text{C}_{10}$ DES is formed at a molar ratio of 1:4, with a melting point of $22\text{ }^\circ\text{C}$. Also, the eutectic mixture has a lower melting point than the corresponding starting materials, yielding a window of compositions in the liquid phase at room temperature. This was found by visual inspection and confirmed by DSC analysis, as presented in thermograms in the ESI.† All the details of the preparation, characterization and thermophysical property measurements of the newly prepared sodium salt-based DES can be found in the ESI.† It can be concluded that the thermophysical properties of the $\text{NaC}_{12}:\text{C}_{10}$ DES, namely density and viscosity, are similar to those reported for the hydrophobic DES, with lower densities and viscosities than hydrophilic DESs.

An important characteristic feature of a hydrogel is its water holding capacity.²⁴ When the $\text{NaC}_{12}:\text{C}_{10}$ DES is put in contact with water, the formation of a hydrogel can be observed. This water holding capacity and its consequent restructuring of the hydrogen bond network is an important characteristic feature of any hydrogel.²⁴

The presence of the charged sodium atoms seems to have a decisive role in the formation of the hydrogel, since in our

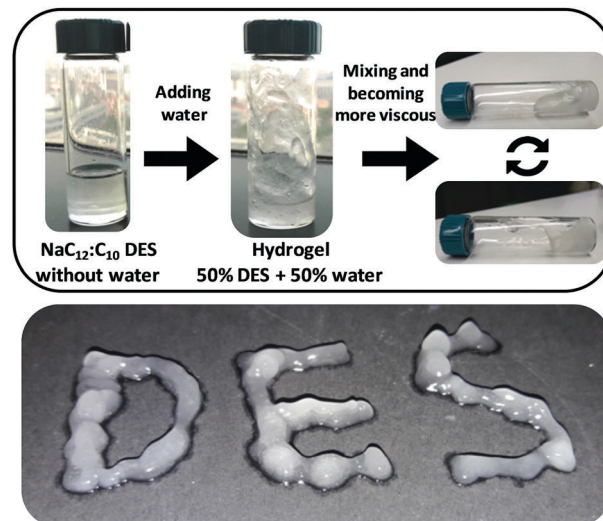


Fig. 2 Illustration of the pure sodium salt-based DES, $\text{NaC}_{12}:\text{C}_{10}$ (1:4 molar ratio) without water and after addition of 50 wt% of water, becoming more viscous and more turbid, forming a gel system. Below, a photograph of the hydrogel composed of 50 wt% of the DES and 50 wt% of water at $25\text{ }^\circ\text{C}$.

previous work the reported DES was formed using two carboxylic acids with a long alkyl chain and complete DES immiscibility with water was observed and, of course, no gel was formed. In the present case, instead of two mutually immiscible liquid phases, a hydrogel was obtained. The more water was added, the more viscous the gel became. Fig. 2 presents an illustration of the formation of the gel system for one selected composition (50 wt% of DES + 50 wt% of water).

In order to better evaluate and understand the behaviour of the $\text{NaC}_{12}:\text{C}_{10}$ DES with water, the (T and x) phase diagram was measured using a visual method and it is shown in Fig. 3.

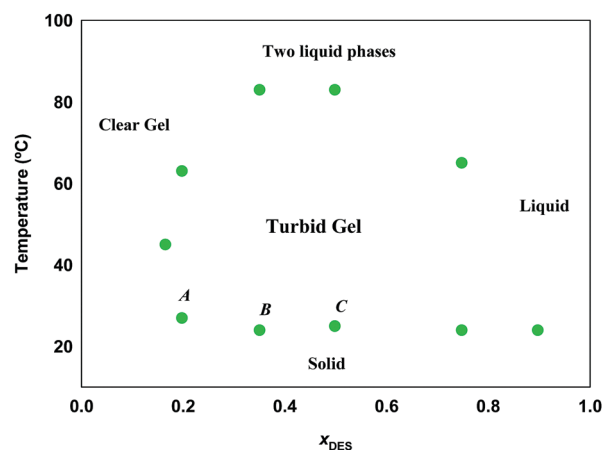
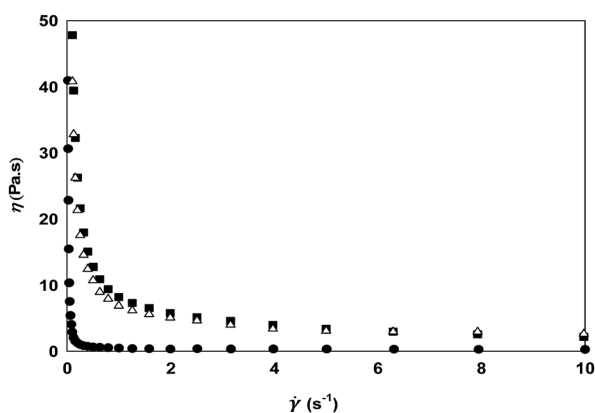


Fig. 3 Temperature-composition sol-gel phase diagram of the sodium salt-based DES aqueous solutions. Green circles (●) indicate the sol-gel transitions of $\text{NaC}_{12}:\text{C}_{10}$ (1:4) for different compositions with temperature. A, B and C correspond to pure DES mole fractions of 0.197, 0.350 and 0.498 and 0.803, 0.650 and 0.502 of water. These A, B and C mixtures were selected for further studies.

1 It can be observed that the mixtures of the NaC₁₂:C₁₀ DES
and water exhibit stimuli sensitive and responsive phase transition to the temperature and concentration of water, probably
5 due to the changes in the network structure.

6 According to Fig. 3, at temperatures slightly above room
temperature, the NaC₁₂:C₁₀ DES + water mixtures might yield
either a clear gel, or a turbid gel or a liquid phase, depending
on DES concentration. The turbid gel, obtained for molar ratios
10 of the DES between 0.30 and 0.70, yields phase separation at
higher temperatures, and two liquid immiscible phases were
obtained. Just like conventional supramolecular hydrogels,
supramolecular hydrogel-based DESs will certainly attract significant
15 interest for their possible use in interesting applications,
such as hygienic products, drug delivery systems,
biomedical applications, sensors and pharmaceuticals, the
removal of dyes and metal ions and sewage water treatment,
and the purification of water, among others.^{24–27}

20 The rheological properties of the hydrogels were also
obtained by investigating the viscometry in rotational mode
and viscoelastic properties in oscillation mode, as well as by
thixotropy and creep/recovery tests. A rotational rheometer
from Malvern (Kinexus pro) was used with a cone-and-plate
geometry. The measurements were carried out for three binary
mixtures of different compositions A, B and C, which correspond
25 to a DES molar fraction of 0.197, 0.350 and 0.498 DES
and 0.803, 0.650 and 0.502 of water, respectively, as marked
in Fig. 3, and two different temperatures within the gel region
of the phase diagram. These hydrogels are markedly non-newtonian
materials, exhibiting shear thinning behaviour, as can be seen
30 in Fig. 4, whose flow curves (Fig. ESI8 in the ESI†) can be
correlated with the Herschel–Bulkley model with a flow consistency
index (K), a flow behaviour index (n) and a yield stress (τ_0) quite
dependent on composition (Table ESI2 in the ESI†). The application
of high strains on the systems seems to easily break their gel
35 structure leading to sol phase formation. Mixture C was particularly
fragile exhibiting the lowest consistency index, almost a negligible
yield stress and the most marked shear thinning behaviour, with
the lowest viscosity values for a given shear rate. Mixtures A and
B showed a similar behaviour.



55 Fig. 4 Viscosity (η) as a function of shear stress for three gel compositions
with angular speed (ω) for composition A (Δ), B (\blacksquare) and C (\bullet) at 40 °C.

1 The gel behaviour of the systems could be clearly seen in the
oscillation tests, where the elastic module (G') is consistently higher
than the viscous module (G''), as presented in Fig. 5, with no cross-
over detected in the frequency range imposed (0.01–100 s⁻¹) for low
5 strains and phase angles always less than 15°. However, these gels
should be classified as weak, which can be seen by the shear
thinning behaviour in the flow tests (high strains) and the relatively
narrow linear viscoelastic regimes (strains between 0.2 and 1%).

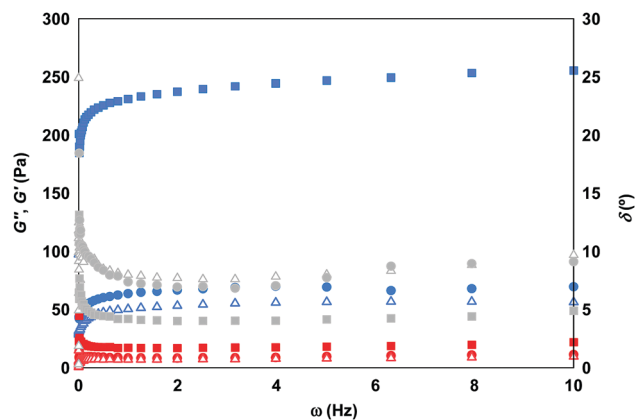
6 Another indication of the viscoelastic behaviour of these
hydrogels is the results of the creep/recovery tests at a constant
shear stress (sufficiently low not to break up the gel structure)
which are shown in Fig. ESI11 in the ESI.†

7 Comparing the shear moduli obtained for the three studied
compositions, it seems that these mixtures do not present a
monotonic behaviour as a function of composition. This fact is
also visible from the viscosity measurements as a function of
10 the shear rate. A more detailed study on the composition
dependence of the rheological properties of these gels will be
carried out to elucidate this point.

8 After the steady state was attained, removing the stress
allowed the gels to spring back, with an ultimate recoil value
of 0.0302 Pa⁻¹ for a maximum creep compliance of 0.0595 Pa⁻¹
[ω (DES) for composition A] and 0.342 Pa⁻¹ for a maximum
15 creep compliance of 1.469 Pa⁻¹ [ω (DES) for composition C].
The fact that both values of ultimate recoil are non-zero,
representing a fraction of 0.51 (A) and 0.23 (C) of the maximum
compliance, proves the significant spring back of the samples
when stress is removed due to their elastic character (typical
20 of gels).

9 The oscillation experiments in temperature sweep mode for
fixed strain and oscillation frequency, allowed us to detect
the low temperature limit of the gel phase corresponding to
the point where a steep increase in storage module occurs,
as can be seen in Fig. 6 for the mixture with composition
25 A for which the phase transition temperature was found to
be 16 °C.

10 Finally, these hydrogels proved to be thixotropic as can be
observed from the results of the creep/recovery tests shown in



55 Fig. 5 Oscillation experiments in frequency sweep mode for gel mixtures
with angular speed (ω) for composition A (Δ), B (\blacksquare) and C (\bullet) at 40 °C
(— storage module (G'), — loss module (G'') and — phase angle (δ)).

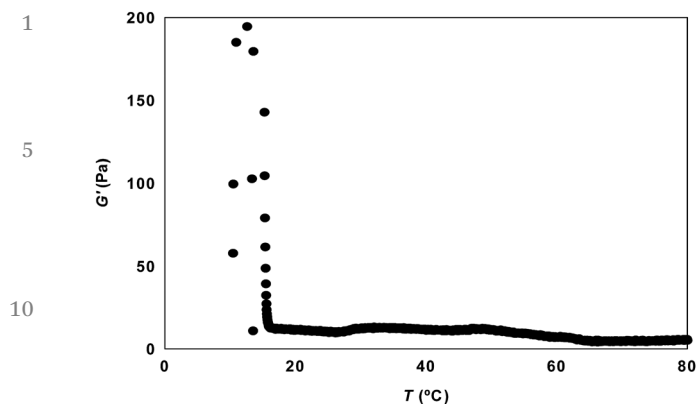


Fig. 6 Oscillation experiments in temperature sweep mode for the gel mixture with the angular speed (ω) of the DES mixture with composition A for an oscillation frequency of 1 Hz and a strain of 0.1%. Storage module as a function of temperature.

Fig. ESI12 in the ESI.† At constant low shear rates, the apparent viscosity decreases with time. Upon the application of higher shear rates, the viscosity deeply decreases (breaking of the gel structure). However, once the high shear rate is removed, these gels present low rebuild times, which is an indication of the reversibility of the gel breaking process. Both the decrease of viscosity with time at constant shear rates and the rebuild of the original structure in a finite time show the thixotropic nature of these gels.

For the first time a new metal-based DES, combining a dodecanoate sodium salt as a HBA and a carboxylic acid as a HBD, that can behave as a hydrogel in the presence of water was reported. This new hydrogel exhibits a temperature phase transition, and also thermoreversible viscosity depending essentially on the water content.

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Conflicts of interest

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