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Electronic Supplementary Information

Metallo Supramolecular Hydrogel based on a Sodium Deep Eutectic Solvent

Catarina Florindo,[a,b] Lucas G. Celia-Silva[b,c], Luís F. G. Martins[b,c], Luís C. Branco[d] and Isabel M. Marrucho[a,b*]

[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, Portugal*

[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*

[d]*REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal*

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[*] Corresponding author. Tel.: +351 218413385; fax: +351 218499242. E-mail address: isabel.marrucho@tecnico.ulisboa.pt (I. M. Marrucho).

ESI1: Experimental details

Materials. Dodecanoate sodium salt (NaC_{12}) (purity 99-100%) and decanoic acid (C_{10}) (purity ≥ 98%) were purchased from Sigma-Aldrich. All materials were used without further purification. The water used was ultrapure; double distilled, passed through a reverse osmosis system and further treated with Milli-Q plus water purification apparatus.

Preparation Methodology of DES. Mixtures of sodium salt and carboxylic acid with long alkyl chain, in a proportion of 1 to 4 of mole ratio, respectively, were prepared by adding the acid to the sodium salt in a sealed glass vial until a homogeneous clear solution was formed. The water content of DES after its preparation and after drying was found to be about 3000 ppm and 280 ppm, respectively. These results were obtained by Karl Fischer titration (Metrohm 870 KF Titrino Plus). The influence of sodium ion on the DES behavior towards water was not evident during the synthesis of DESs since both dried DES (NaC12:C10 and C12:C10) had approximately the same amount of water (150 to 200ppm). However, a clear difference can be observed in the study of DES hydrophobicity: one (C12:C10) gave rise to a two phase system, displaying a very hydrophobic behavior with a maximum water content of 5000 ppm, while the other (NaC12:C10) formed a more viscous phase giving rise to the gel system.

Preparation of the Hydrogel. After the synthesis of a mixture composed of a dodecanoate sodium salt and decanoic acid (1:4 mole ratio), the hydrogel was achieved by homogeneously mixing different amounts of DES and water, from 10 to 80wt%, at 25 °C.

Solid-liquid phase diagram determination. The phase diagram was measured in a glass flask using the visual method at atmospheric pressure, under constant stirring and at different temperatures. Briefly, to perform this experiment it was started with pure compounds HBA and HBD and then made mixtures in varying molar proportions into several glass flasks. Each one of these mixtures, plus the pure HBA and pure HBD represent different compositions, as can be seen in Figure ESI1. In this case, we only evaluated the temperature at which the solid-liquid transition occurs for different DES compositions, holding pressure constant at 1atm. The eutectic systems compositions were determined by weight quantification of all components within ± 10^{-4} g.

The eutectic composition was obtained at only one temperature, the lowest melt temperature when compared to the starting materials. The above procedure was repeated to obtain sufficient data to construct the phase diagram of the studied DES, shown in Figure ESI1.

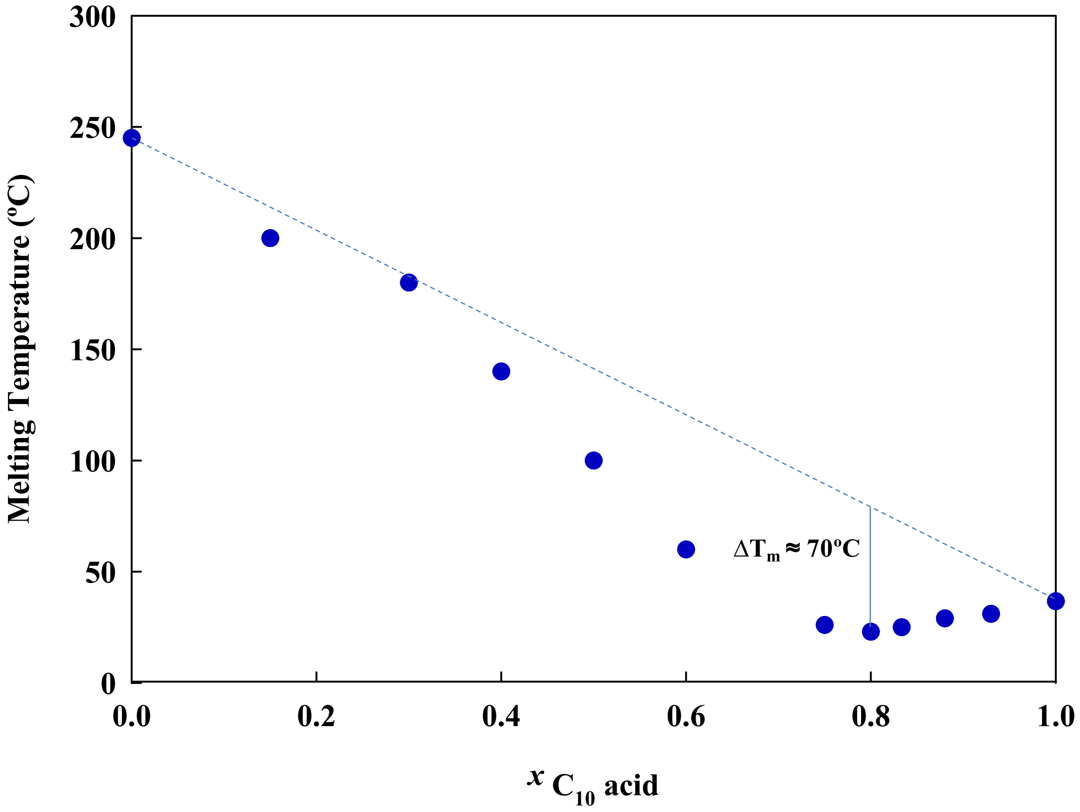

Figure ESI1. Experimental (T,x) phase diagram obtained for NaC12:C10 DES.

Sol-Gel phase diagram determination. The sol–gel phase transition temperature for the hydrogel was determined using a vial containing different mass proportions of DES and water, as can be seen in Figure 3, in an oil bath with constant stirring speed with a temperature increment of 5 °C. The appearance of the gel state was determined by visual observation of the change in the fluidity when temperature changes. The temperature was measured with a precision of ± 1 °C.

ESI2: Analytical Methodologies

Karl-Fischer measurements. In order to measure the quantity of water of DES after the preparation and drying, a Karl Fischer titration analysis (Metrohm 870 KF Titrino Plus) was used.

Thermophysical Properties. Measurements of viscosity and density of the DES were carried out in the temperature range from 20 up to 80 ^{o}C and at atmospheric pressure, using an Anton Paar (model SVM 3000) automated rotational Stabinger viscometer-densimeter. The temperature uncertainty is ± 0.01 ^{o}C. The relative uncertainty of the dynamic viscosity is ± 0.25 %, and the absolute uncertainty of the density is ± 0.0005 $g\cdot cm^{-3}$. A DSC (differential scanning calorimeter TA Instrument Model DSC Q200) was used to measure the thermal properties of the prepared DES. In the DSC, the samples were continuously purged with 50 mL min−1 of nitrogen. About 10 mg of the compound was crimped in an aluminum standard sample pan and analyzed under a nitrogen atmosphere by heating (10 K min −1)− cooling (5 K min −1) cycles between 193.15 and 373.15 K.

FTIR analysis. FTIR measurements were carried out using a Brüker IFS66/S FTIR spectrometer (Brüker Daltonics, MA, USA) with a single reflection ATR cell (DuraDisk, equipped with a diamond crystal). The data relative to spectral region were recorded between 4000 cm-1 and 600 cm-1 at room temperature. For each sample, 290 scans were recorded at a spectral resolution of 4 cm-1 and five replica spectra were collected in order to evaluate reproducibility (OPUS v5.0).

Rheological Properties. Rheological studies comprised viscometry measurements in rotational shear rate controlled mode (in general for shear rates between 0.001 and 100 s^{-1}), viscoelastic tests in oscillation mode using strain (for linear viscoelastic region – LVER), frequency (in general, frequency between 0.01 and 100 s^{-1}) and temperature (single frequency) sweep, creep/recovery and thixotropy tests. All the measurements were made in a Kinexus pro rotational rheometer from Malvern with cone and plate geometry (cone with 40 mm of diameter, an angle of 4^{o} and a gap of 0.15 mm). Temperature was controlled by a Peltier element at the bottom of the fixed plate and measured with a precision of 0.01 ^{o}C. The systems studied were gels with 0.803, 0.650 and 0.502 weight fractions of water at 40 and 60 ^{o}C.

ESI3: FTIR Analysis

As already proven, different intermolecular interactions are responsible for the formation of a eutectic mixture, depending on the compounds. In conventional DES based on a salt and a carboxylic acid, which acts as hydrogen bond acceptor and donor, respectively, the establishment of hydrogen bonds between the two compounds is responsible for the eutectic solvent formation. Thus, it is important to observe how dodecanoate sodium salt interacts with decanoic acid, in the DES prepared in this work. For that purpose, FTIR experiments were performed for the pure starting materials, dodecanoate sodium salt and decanoic acid, and the DES. The FTIR spectra obtained are presented in Figure ESI2.

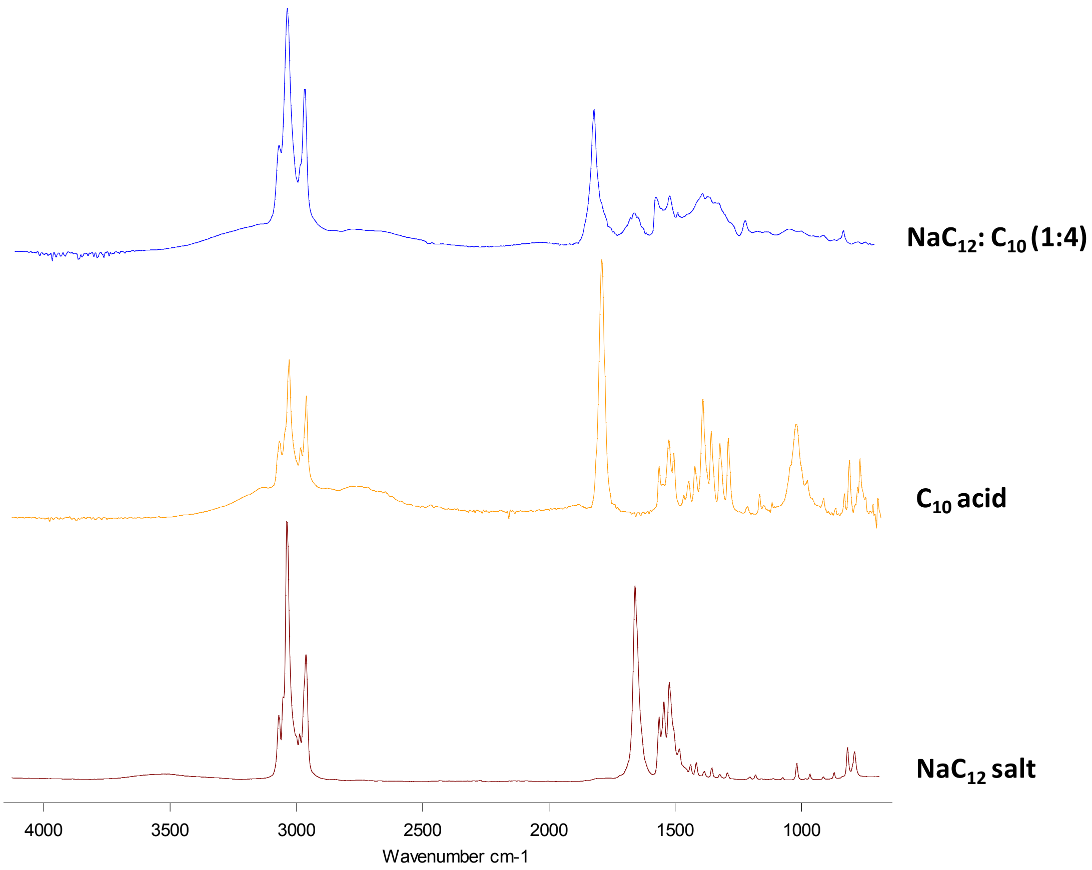

Figure ESI2 – FTIR spectra of the pure dodecanoate sodium salt (NaC_{12} salt), decanoic acid (C_{10} acid) and NaC_{12}: C_{10} (1:4 mole ratio) DES.

FTIR analysis is also used to confirm the formation of the new compound, through the establishment of hydrogen bonds, between the salt and the hydrogen bond donor. As can be seen from the Figure ESI3, an intermolecular hydrogen-bond interaction between the hydrogen bond donor and the salt, mostly in the carboxyl group region, is formed. It can be observed that the carbonyl band from the HBD was originally located at lower wavenumber values (~1700 cm-1) and it broadens and shifts to higher values (~1750 cm-1) in the eutectic mixture. This is a strong indication of a new hydrogen bond formation, thus proving that a new compound was formed. This evidence can be further confirmed through the physical state of the compounds: initially, the physical state of both these compounds was solid and after DES formation an homogeneous liquid is obtained at room temperature.

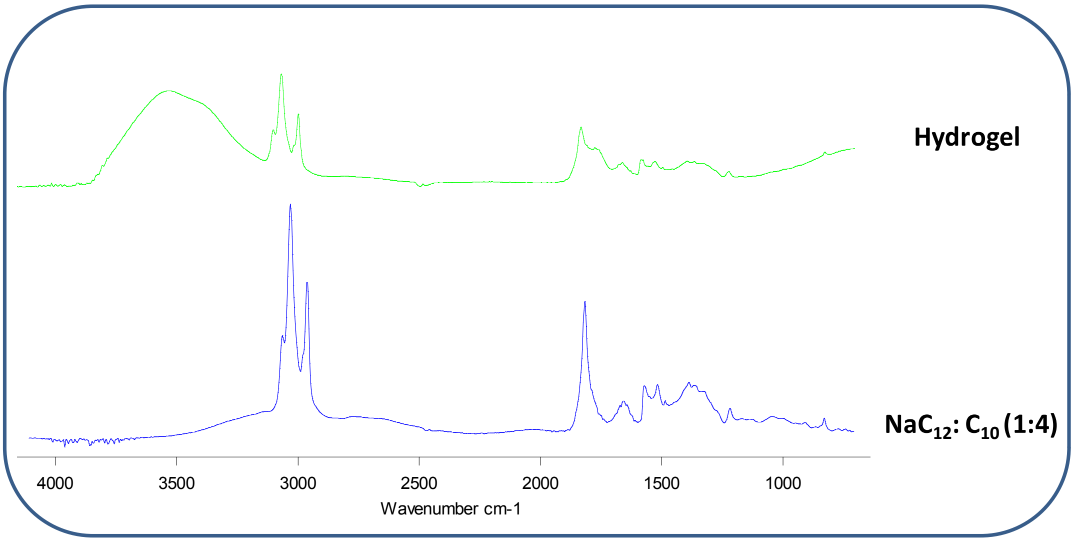

Figure ESI3 – Comparison of FTIR spectra of the sodium salt-based DES (NaC_{12} salt) without water and the corresponding hydrogel (50wt% DES of NaC_{12}: C_{10} (1:4 mole ratio) and 50wt% of water).

ESI4: DSC analysis of DES and Hydrogel

The new NaC_{12}:C_{10} DES and the corresponding hydrogel (50% of DES and 50% of water) were also characterized using differential scanning calorimetry (DSC). In order to prove the eutectic behaviour of this new system, in Figure ESI4, a comparison of DSC thermograms between the pure sodium salt-based (NaC_{12}:C_{10}) and the pure decanoic acid (C_{10} acid) starting material is presented.

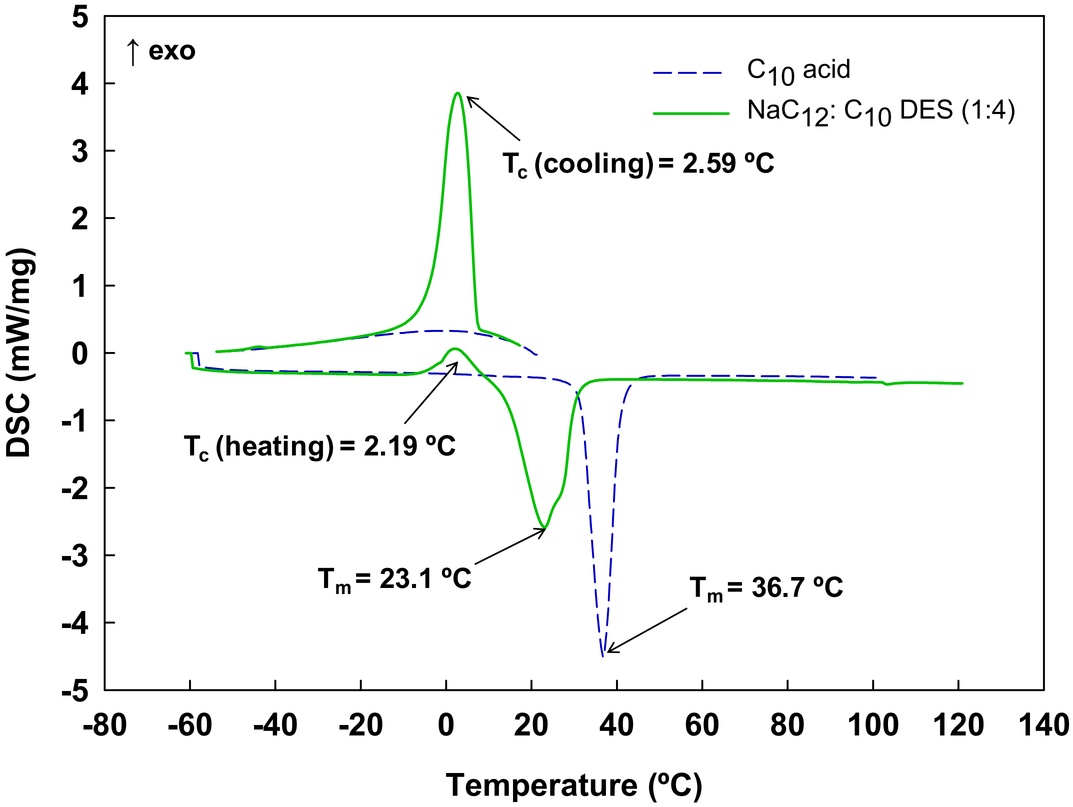

Figure ESI4 – Comparison of DSC thermogram between the pure sodium salt-based (NaC_{12}:C_{10}) and the pure decanoic acid (C_{10} acid) starting material. (Note: Due to the limitations of the equipment, it was not possible to measure the melting point of the initial material (dodecanoate sodium salt), although this is well defined in the literature and in the safety data sheet, being at 245 °C.)

As can be seen in Figure ESI4, there is a difference in melting temperatures of both pure compounds and the DES: sodium dodecanoate salt and decanoic acid have a melting point of 245 °C and 36.7 °C, respectively, and DES in a mole ratio of 1:4 presents a melting point of 23.1 °C. DES (NaC_{12}:C_{10} (1:4)) also presents a cold crystallization at 2.59 °C and a heat crystallization at 2.19 °C, which does not occur for the starting material.

These results are in agreement with those obtained by visual inspection of the melting points and that are reported in the (T, x) phase diagram in Figure ESI1: a lowering of ≈70 °C in the melting temperature of the DES compared that which should be obtained for a ideal mixtures is observed.

In Figure ESI5, DSC thermograms of hydrogel composed of 50wt% of DES and water and the pure corresponding DES are presented and compared.

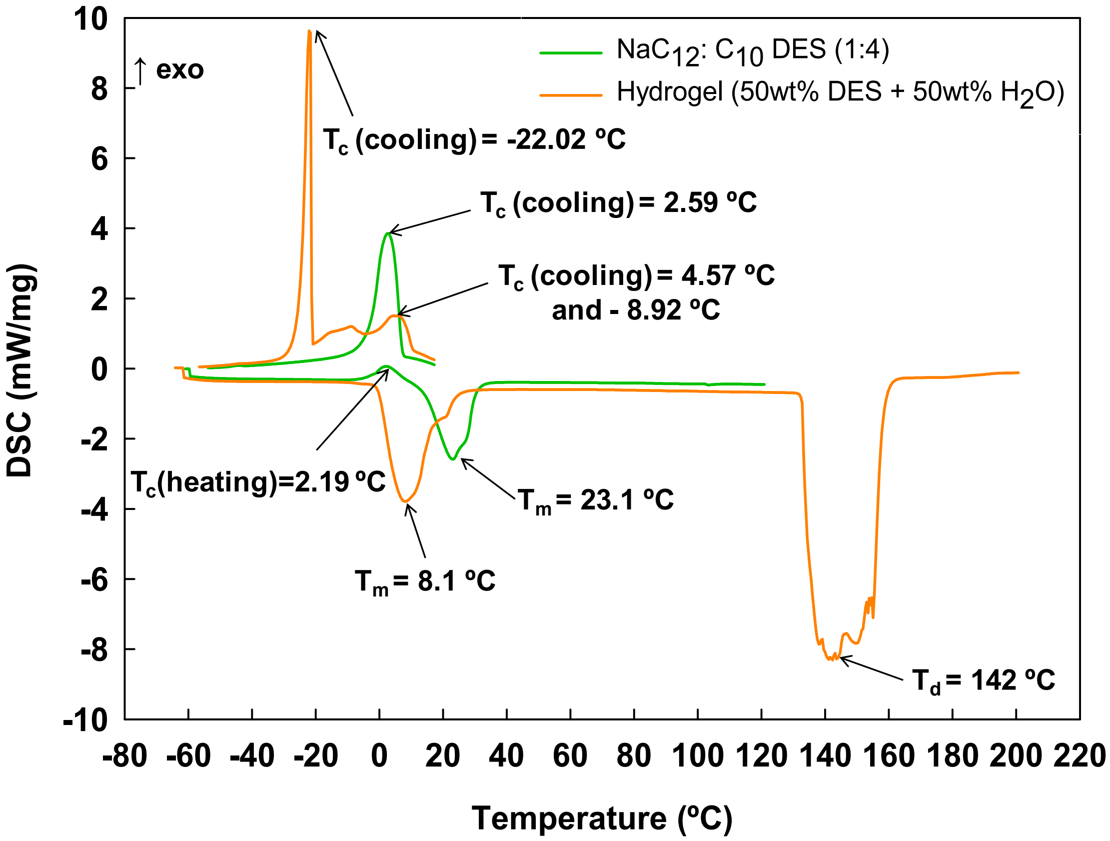

Figure ESI5 – Comparison of DSC thermogram of the pure sodium salt-based DES (NaC_{12} salt) and the corresponding hydrogel (50wt% DES of NaC_{12}: C_{10} (1:4 mole ratio) and 50wt% of water).

Regarding results, it can be seen that hydrogel showed a completely different pattern on thermogram from DES. From DSC thermogram of hydrogel it is possible to see the different transition phases as well as showed the degradation of the polymeric network at 142 °C and possible evaporation of water, after the melting temperature of the hydrogel. DES and hydrogel have a melting temperature of 23.1 and 8.1 °C, respectively, as a difference of 15 °C between them. However, this is expected since water has a melting point lowering effect, and the hydrogel present an amount of 50wt% of water in their composition. Also in the DES profile can be seen the existence of heat crystallization at 2.19 °C, which disappears when it becomes a hydrogel and stores water in its polymer network. Finally, regarding cold crystallization, it can be seen that both systems present them, but again with very different profiles: DES presents one big and isolated cold crystallization at 2.59 °C and hydrogel presents three different cold crystallizations, a large and thin one at -22.02 °C and two smaller and wider at 4.57 and -8.92 °C. From all data present in these DSC thermograms, it can be concluded that the chemical structure of hydrogel is much more complex than that presented by DES.

ESI5: Thermophysical properties, densities and viscosities

Density and viscosity are important properties of any solvent since they influence the mass transport phenomena, there by affecting their suitability for particular applications. The density decreases linearly with temperature for all dried samples, in the whole temperature range studied. A linear equation was used to express the correlation with the temperature:

$$\rho = \mathrm{a} + \mathrm{b}\mathrm{T} \qquad \text{(eq. 1)}$$

where ρ corresponds to density in g·cm^{-3}, T is the temperature in ºC and a and b are the fitting parameters.

The experimental viscosity values were fitted as a function of temperature, using the Vogel-Fulcher-Tammann (VFT) model using the following equation:

$$\ln \eta = A_\eta + \frac{B_\eta}{(T - C_\eta)} \qquad \text{(eq. 2)}$$

where η is the viscosity in mPa·s, T is the temperature in ºC, and A_η, B_η, and C_η are adjustable parameters. The experimental density and viscosity results for the dried DES as a function of temperature are presented in Table ESI1 and in Figure ESI7.

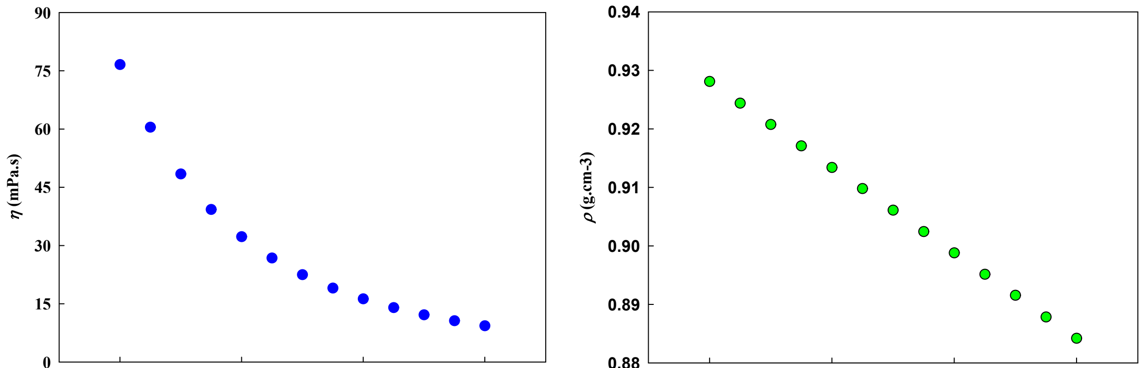

Figure ESI7. Viscosity (η (mPa.s))and density (ρ (g·cm-3) data obtained for the NaC$_{12}$: C$_{10}$ acid (1:4) DES.

Table ESI1. Experimental density, ρ (g·cm^{-3}), and viscosity, η (mPa·s), of the dried NaC12:C10 DES as function of temperature (T/°C).

T (°C)	ρ (g·cm^{-3})	η (mPa·s)
20	0.928	76.59
25	0.924	60.48
30	0.921	48.43
35	0.917	39.29
40	0.913	32.27
45	0.910	26.79
50	0.906	22.48
55	0.902	19.04
60	0.899	16.27
65	0.895	14.02
70	0.892	12.16
75	0.888	10.63
80	0.884	9.346

ESI6: Rheological properties

Flow curves (shear rate between 0.005 and 10 s^{-1}) for three gel samples at 40 °C are presented in Figure ESI9. For shear rates above 10 s^{-1} some mixtures become unstable.

The flow curve was fitted to Herschel-Bulkley model:

$$\tau = \tau_0 + K\dot{\gamma}^n \qquad \text{(eq. 3)}$$

with *K* being the consistence index, *n* the flow behaviour index and T_0 the yield stress, and the obtained parameters are presents in table ESI2.

Table ESI2. Flow consistence index (*K*), flow behaviour index (*n*) and yield stress (τ_0) for three gel mixtures.

Mixture	*K* (Pa.s^n)	*n*	τ_0 (Pa)
ω (DES) for composition A	3.56	0.81	3.38
ω (DES) for composition B	5.53	0.56	3.34
ω (DES) for composition C	0.30	0.89	0.17

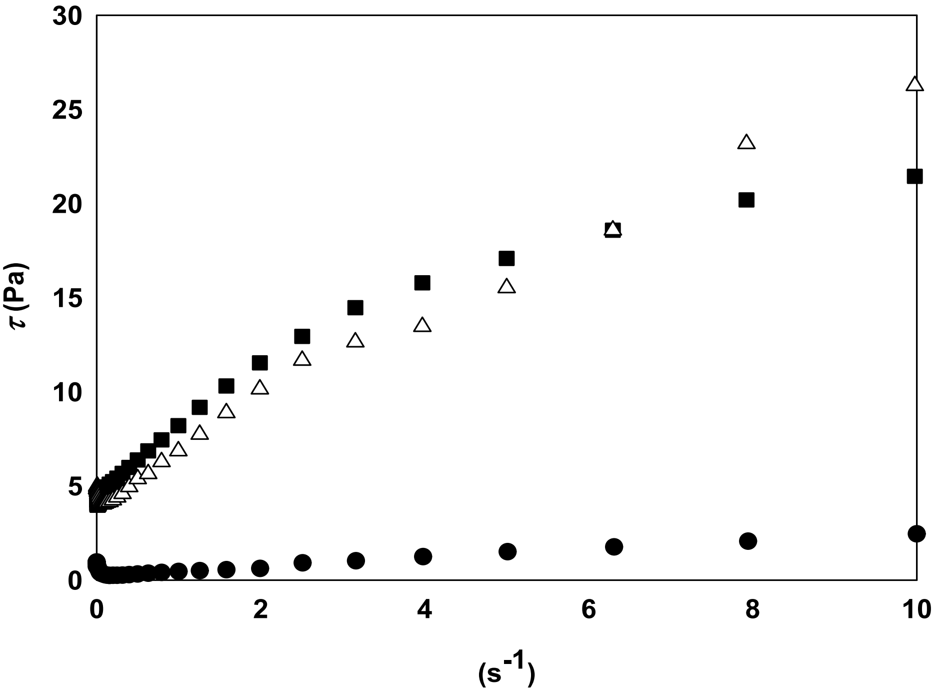

Figure ESI8. Flow curves (shear stress as a function of shear rate) for three gel mixtures with ω (DES) for composition A (Δ), B (■) and C (●) at 40 °C.

In figure ESI9, viscosity as a function of shear rate for gel mixture with *ω* (DES) for composition A at 40 ºC and 60 ºC is shown.

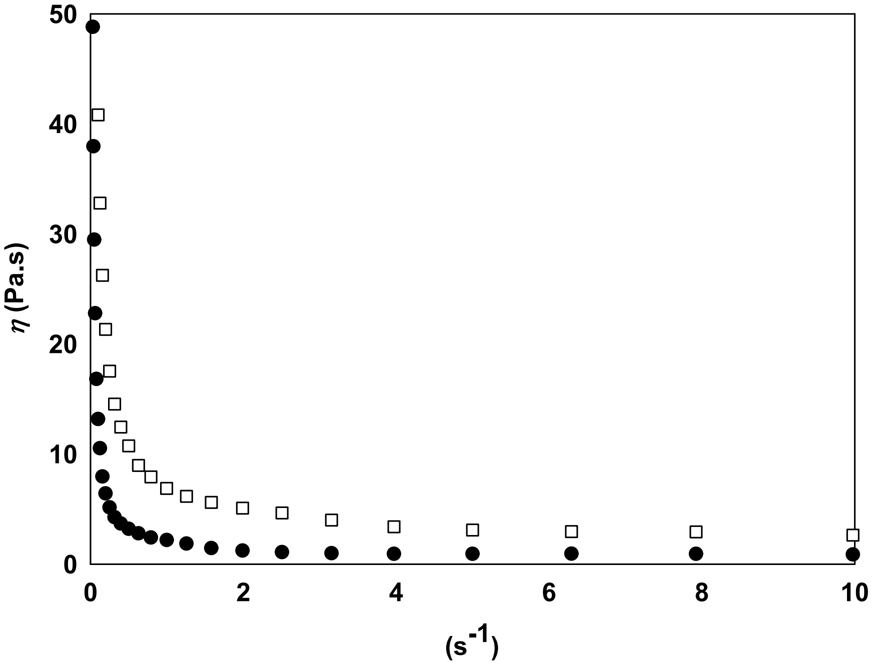

Figure ESI9. Viscosity as a function of shear rate for the gel mixture with ω(DES) composition A, at 40 ºC (☐) and 60 ºC (●).

The viscoelastic properties of gels were studied, first of all, by oscillation experiments with strain sweep, where linear viscoelastic regime (LVER) was obtained (Figure ESI10). From these results, strain values between 0.08 and 1 % were chosen for the remaining oscillation experiments, in order to ensure that the samples are kept in linear viscoelastic regime.

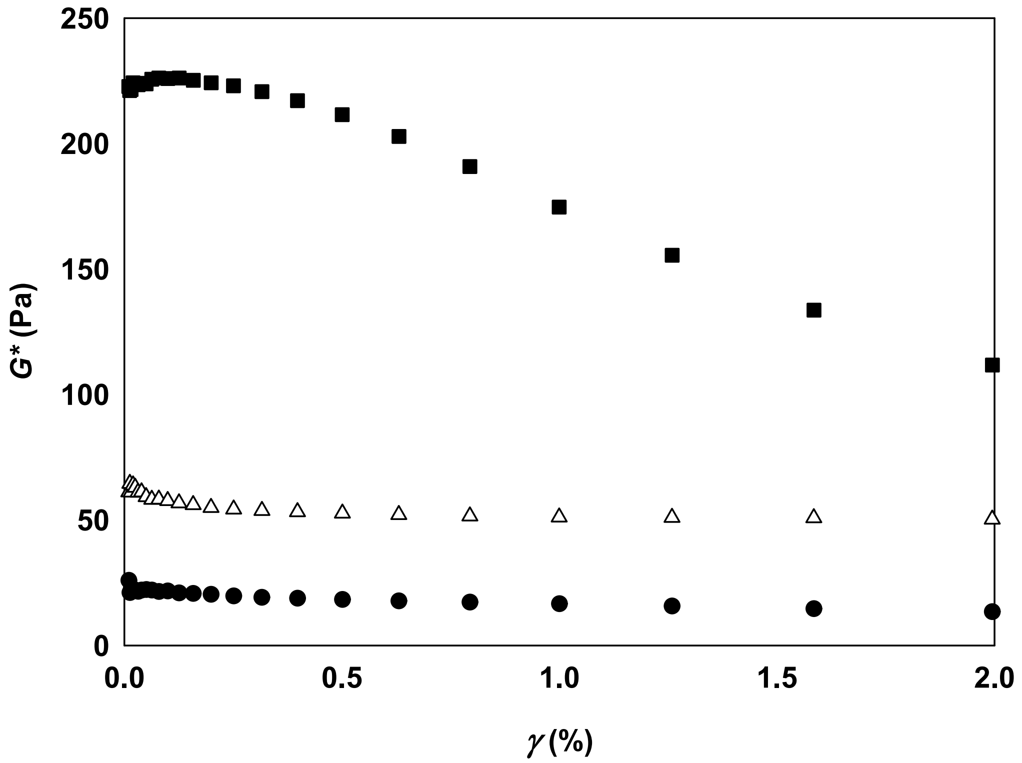

Figure ESI10. Oscillation experiments on strain sweep mode (complex module as a function of strain) for gel mixtures with ω(DES) for composition A (Δ), B (■) and C (●) at 40 °C.

The creep/recovery tests were carried out at low shear stresses (0.4 to 0.5 Pa) and are shown in Figure ESI11 for two gel mixtures.

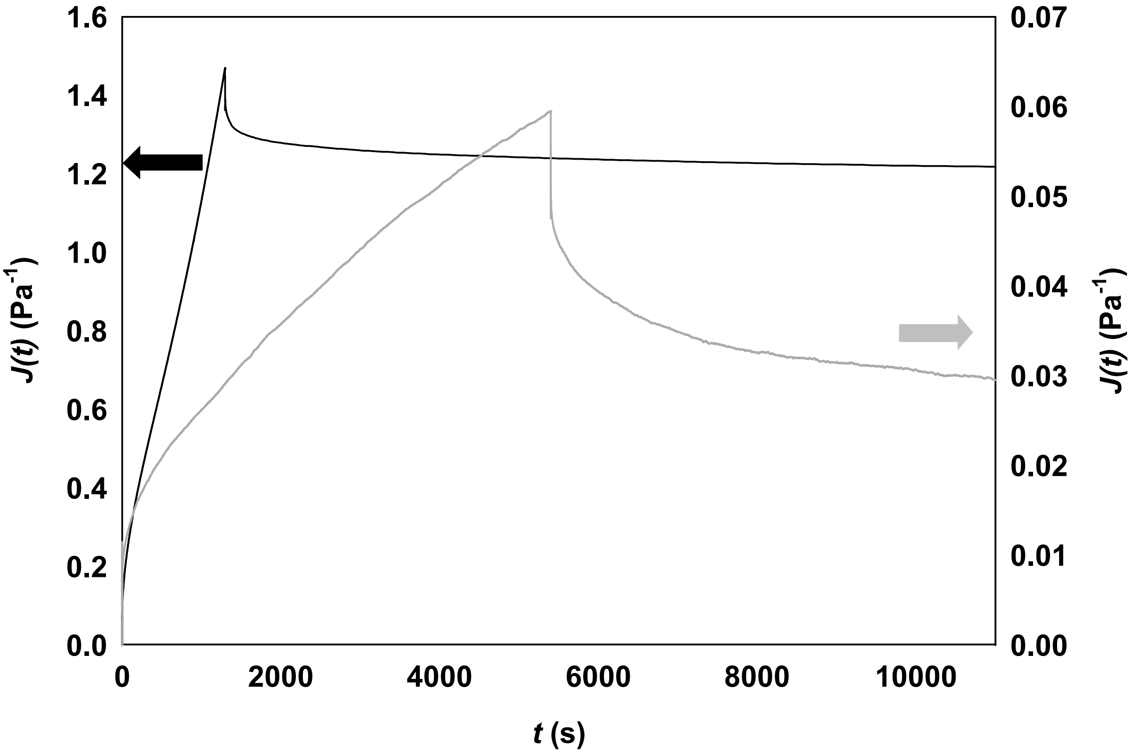

Figure ESI11. Creep/recovery tests. Shear compliance as a function of time for gel mixtures with ω(DES) equal to 0.197 for composition A (grey), and 0.498 C (black) at 40 ºC.

In Figure ESI12, the thixotropy test for one gel mixture is shown for which shear rates of 0.01 s^{-1} (lower) and 25 s^{-1} (higher) were used. A rebuild time of 486 s was obtained.

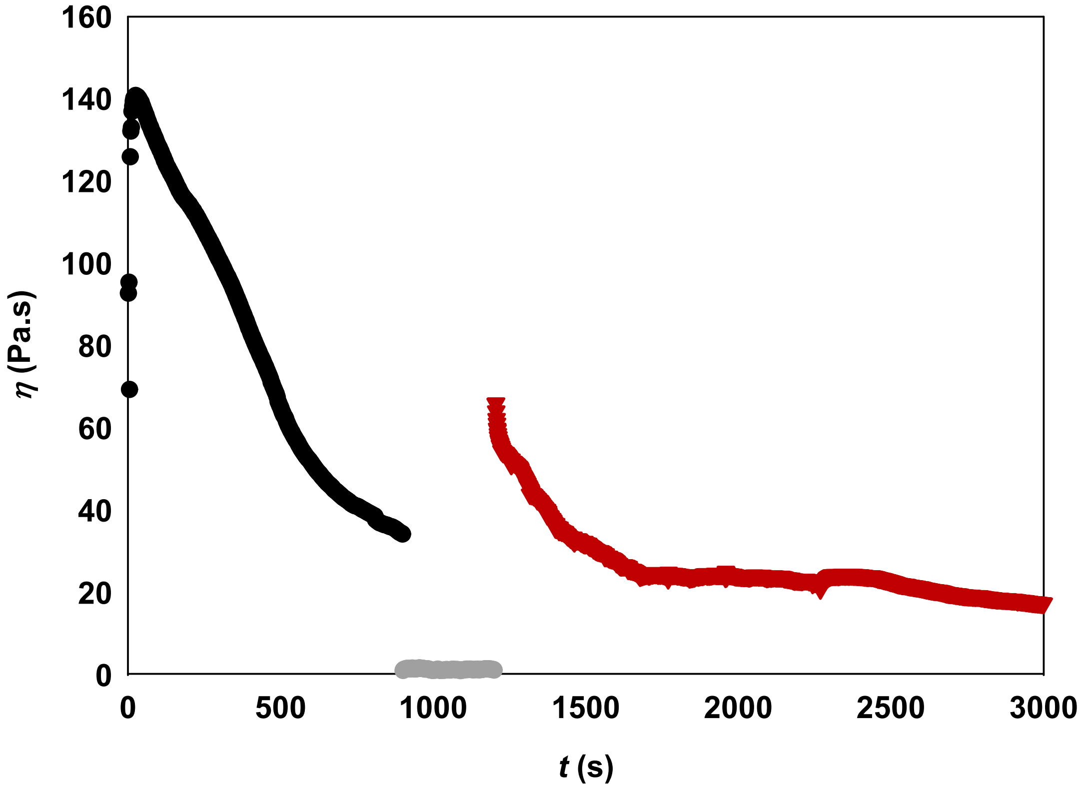

Figure ESI12. Thixotropy test for gel mixture with ω (DES) for composition A at 40 ºC; Viscosity as a function of time for shear rates equal to 0.01 s^{-1} (▬ and ▬) and 25 s^{-1} (▬). Structure rebuild: ▬.